Early transition metal complexes supported by silanol and crown ether substrates

Rainford, Christopher Charles

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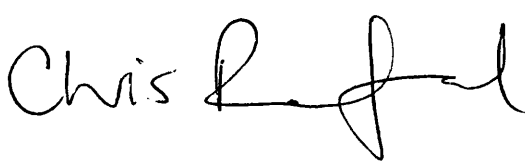
Early Transition Metal Complexes Supported By Silanol and Crown Ether Substrates

Submitted by **Christopher Charles Rainford**

for the degree of PhD

of the University of Bath 1997



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For Raymond,

REMEMBER

Remember me when I am gone away,
Gone far away into the silent land;
When you can no more hold me by the hand,
Nor I half turn to go yet turning to stay.
Remember me when no more day by day
You tell me of our future you planned:
Only remember me; you understand
It will be late to counsel or pray.
Yet if you should forget me for a while
And afterwards remember, do not grieve:
For if the darkness and corruption leave
A vestige of the thoughts that I once had,
Better by far you should forget and smile
Than you should remember and be sad.

Christina Rossetti

Rejoice O young man

in thy youth ...

Ecclesiastes

Acknowledgements

As I write these acknowledgements I am reminded of a short excerpt from the epilogue of Hemmingway's Death in the Afternoon.

> The great thing is to last and get your work done and see and hear and learn and understand; and write when there is something that you know; and not too damned much after. The thing to do is work and learn to make it.

Joe Simpson later used the passage to describe his traumatic experiences in the mountains but what is written here represents what I have seen, heard, learnt and understood during my last three years in the laboratory. Although the crests and troughs are vastly different to Simpsons I empathize with his sentiments. I too have made it, ... I think.

I have had a great deal of support during my study and I am especially grateful to my supervisor Dr Brian Brisdon for the enormous commitment, support and advice that he has so generously furnished me with. I would also like to thank Dr Mary Mahon for the crystallography, Mr Alan Carver for the microanalysis and the rest of the staff of the inorganic chemistry department for their time and help. Though the majority of synthetic work was undertaken alone I would like to raise a big hand to Dr David Smith for his collaboration with the preparation of the aza crown ethers, and to Wendy Davies as well as Mark Harwood for their invaluable contributions to the metallacrown work.

Life for those in the lab will undoubtedly be duller and less demanding without my presence and so to all those who have been involved; Smudge, Sumo, John, Mike, Mr Ron and Mrs Tim, Rob, Jo, Mike, Phil and Virginnie I offer my sincere apologies. I hope that at some time in my future I will again find myself in such esteemed company that the Telegraph quick crossword takes only a day to complete.

Whilst I remained in Bath principally to undertake research for my PhD I look back now over this period of time and realise that much of what I have learnt will remain unwritten in this thesis. Without being articulate or able enough to make sense or explain my experiences over this period I realise that these have been my formative years. The years will drift by so that some of the images I remember now will be tarnished and forgotten but I am confident that it will not diminish the feelings and memories of the good times enjoyed with my friends. In particular the experiences I have shared with three people stand apart from all others and to whom I consider most privileged to have known. To Luke who has had endured me for my entire life at university, Tam for being there when it matters and Wendy for the inspiration to continue the work, my eternal thanks.

It would take too much time to thank all the others who have conspired to help me through the work but Tom, Jason, Catherine, Sam, Lucy, Mike, Hamish, Fergal, Pete, Andy, Paddy, Dr Aly-poohs,

Rachael, Fraser, Tracy, Dougal, Liz, Spud, Tam II, Bev, E, Stan and the lads at Bath cricket club all deserve my thanks.

Finally last but perhaps most importantly I would like to thank my family for all their support and encouragement during my time at university. My parents have made a huge emotional (and needless to say financial) commitment to me and without them this thesis would not have been possible or worthwhile.

Abstract

The aim of this project was to assess the ability of silanol, siloxane, oxo- and aza- crown ether substrates to function as potential supports for a range of catalytically active metal centres. Of particular interest were molybdenum complexes containing metal-metal multiple bonds, and high oxidation state tungsten compounds both of which have potential widespread applications in industrial and biological systems, as well as low oxidation state molybdenum complexes which are widely employed as catalysts in organic synthesis.

Metal-halide metathesis reactions were successfully utilised to attach hard ancillary ligands, including the triphenylsiloxide and diphenylsilanediolate anions, to a number of tungsten(VI) oxo- and dioxo- chloride moieties to afford $[W(O)Cl(OSiPh_3)_3]$, $[W(O)_2(OSiPh_3)_2(TMSO)_2]$, $[W(O)_2(\mu\text{-}OSiPh_3)L]_2$ where L = $OPPh_3$ and DMSO, and $[WO(\mu\text{-}OPh_2SiO)_2]_2$. The highly air and moisture sensitive tungsten siloxides and siloxanes isolated were characterised by microanalysis, IR and multinuclear NMR spectroscopy techniques. An alternative synthetic approach involved the ring opening reaction of the strained cyclosiloxane $[Ph_2SiO]_3$ using $[W(O)Cl_4]$ to give low yields of the spirocyclic tungstasiloxane $[WO\{O(Ph_2SiO)_3\}_2\cdot THF]$. A structural determination of this complex disclosed significant $O(p\pi)\rightarrow M(d\pi)$ interactions [W-O(Si)$_{av}$ 1.879 Å]. The importance of the solvent, and of ring strain within the cyclosiloxane system were demonstrated by the failure to isolate similar products using non-coordinating solvents and a less strained cyclosiloxanes. Preliminary investigations revealed that the molybdenum-molybdenum quadruply bonded complex $K_4[Mo_2Cl_8]$, but not $[Mo_2(O_2CCH_3)_4]$, to undergo partial substitution of the ligands by bidentate silanol and siloxane complexes. Studies were hindered by the low reactivity of the metal precursors and the extremely poor solubility of the resulting products.

Inclusion complexes of silanol compounds have potential applications as models for water-sedimentary interfaces and as sequestering agents for the selective abstraction of harmful organic residues. In this study oxa- and aza- crown ethers were reacted with varying stoichiometries of triphenylsilanol to yield the host-guest complexes $(Ph_3SiOH)_3\cdot$18-crown-6 and $(Ph_3SiOH)_2\cdot$diazacrown which were characterised by IR, microanalysis and multinuclear NMR techniques. The high affinity of crown complexes for water is apparent in the ternary inclusion complexes $(Ph_3SiOH)_2\cdot$18-crown-6$\cdot(H_2O)_2$ and $(Ph_3SiOH)_2\cdot$monoazacrown$\cdot(H_2O)$ which were prepared in this study and characterised by multinuclear NMR spectroscopy and single crystal x-ray diffraction. Structural determinations of these complexes revealed co-ordination of the guest molecules to the crown *via* intermediate water molecules, and in the latter case a direct SiOH···HN interaction. ^{29}Si NMR solution studies show the magnitude of the chemical shifts for triphenylsilanol

host-guest complexes versus the free silanol to be in the order diazacrown > monoazacrown > 18-crown-6 ≈ triphenylsilanol. This has been interpreted in terms of complex stability which is derived from the number and relative basicities of the donor atoms on the oxa- and aza- crown ethers.

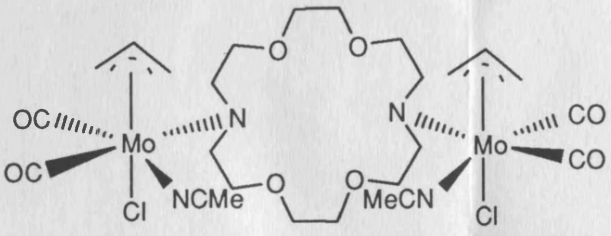
The propensity of $[M(CO)_4(L)_2]$ complexes, where M = Cr, Mo, W, and L = a mono or bidenate ligand, to undergo oxidative addition reactions enables their use as highly efficient catalysts in organic transformations or as isolable intermediates in the formation of metal(allyl)dicarbonyl species. $[Mo_2(CO)_6\cdot(diazacrown)]$ was isolated upon refluxing a toluene solution of $Mo(CO)_6$ in the presence of an equimolar amount of diazacrown. The poor solubility of the product prevented identification of the metal species as either two independent $Mo(CO)_3$ units, or a single metal-metal multiply bonded unit. Attempts to generate analogous chromium and tungsten complexes using this method failed. The successful isolation of a *cis*-$[Mo(CO)_4\cdot(diazacrown)]$ moiety was instead achieved by direct reaction of $[Mo(CO)_4(C_7H_8)]$ with a dichloromethane solution of diazacrown. Metal(allyl)dicarbonyl species are also catalytically active, and their ability to undergo ligand displacement reactions with oxa- and aza- crown ethers, and aza crowns was investigated. Attempts to replace the labile acetonitrile ligands of $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$ with 18-crown-6 or with one or two equivalents of 1-aza-18-crown-6 were unsuccessful. However $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$ readily replaced a single acetonitrile group upon addition of an equimolar amount of 7,16-diaza-18-crown-6 to generate the 2:1 host-guest complex $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)]_2\cdot(diazacrown)$. Earlier studies had revealed a one pot synthesis using $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)]$, 1,4,7-triazacyclononane and NH_4PF_6 to displace the chloride group and both acetonitrile ligands in producing $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(triazacrown)]^+PF_6^-$. These results are indicative of the ability of macrocycles containing "softer" nitrogen donors to form stable complexes with low oxidation state molybdenum species.

Contents

Abbreviations

Å	Ångstrom
acac	2,4-Pentanedionate anion (acetylacetonate anion)
asym	Asymmetric
bipy	2,2'-Bipyridine
br	Broad
Bu	Butyl
c-	Cyclo
C.I.	Chemical ionisation
COD	1,5-Cyclooctadiene
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
Cpd	Compound
CVD	Chemical vapour deposition
d	Doublet
DCM	Dichloromethane
DME	1,2-Dimethoxyethane
DMF	N,N-dimethylformamide
DMSO	Dimethylsulfoxide
dppe	1,2-Bis(diphenylphosphino)ethane
E.I.	Electron ionisation
Et	Ethyl
FAB	Fast atom bombardment
FT	Fourier transform
F-T	Fischer-Tropsch (process)
^{i}Pr	*iso*-Propyl, $CH(CH_3)_2$
IR	Infra-red (spectroscopy)
m	Multiplet
mcpba	*meta*-Chloroperbenzoic acid
m/e	Mass to charge ratio
mes	Mesityl
MeCN	Acetonitrile
MeOH	Methanol
MOCVD	Metal-organic chemical vapour deposition

Mpt	Melting point
NMR	Nuclear magnetic resonance (spectroscopy)
NOE	Nuclear Overhauser effect
OPPh	Triphenylphosphine oxide
Ph	Phenyl
POSS	Polyhedral oligosilsesquioxanes
POMSS	Polyhedral oligometallasilsesquioxanes
ppm	Parts per million
py	Pyridine
Pr	Propyl
q	Quartet
R	Alkyl
s	Singlet
silox	Tri-*tert*-butylsiloxide or silox ,$[(CH_3)_3C]_3SiO$,
sym	Symmetric
T_1	Spin-lattice relaxation time
t	Triplet
^{t}Bu	*tert*-Butyl, $C(CH_3)_3$
THF	Tetrahydrofuran
THP	Tetrahydropyran
tmen	N,N,N',N'-tetramethylethylenediamine
TMEDA	see tmen
TMS	Tetramethylsilane
TMSO	Tetramethylenesulfoxide
Tosylate	*para*-Toluenesulphonyl, p-$CH_3C_6H_4SO_2$-
Tritox	Tritox, $\{(CH_3)_3C\}_3CO$
Trif	Triflate, OSO_2CF_3
Ts	Supermesityl
XPS	X-ray photoelectron spectroscopy
18-crown-6	1,4,7,10,13,16-Hexaoxacyclooctadecane
1-aza-18-crown-6	1,4,7,10,13-Pentaoxa-16-azacyclooctadecane
7,16-diaza-18-crown-6	1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane



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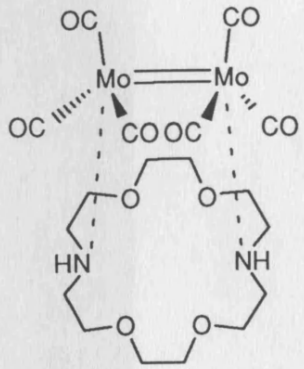

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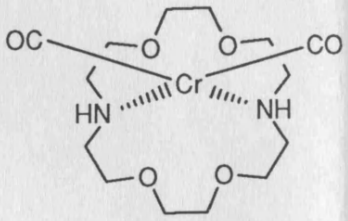

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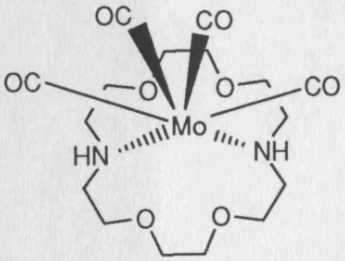

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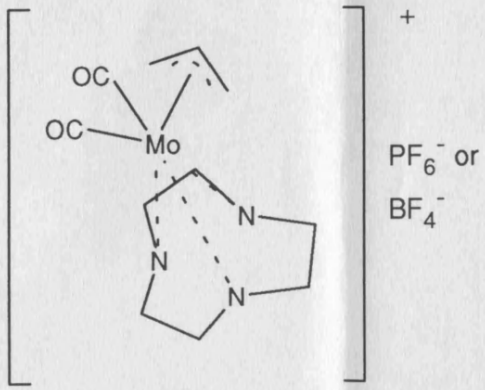

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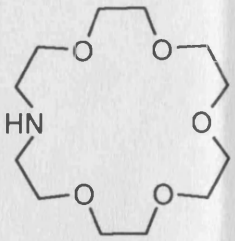

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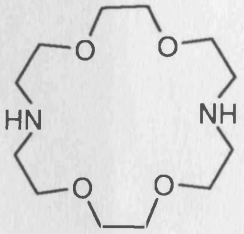

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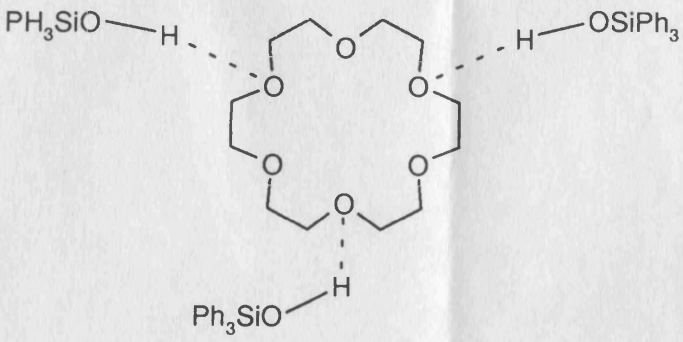

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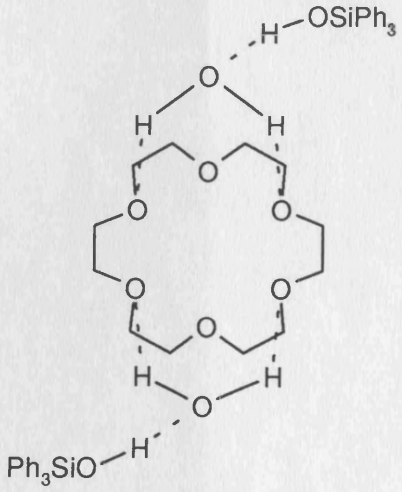

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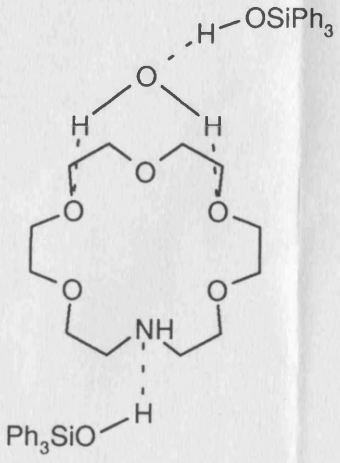

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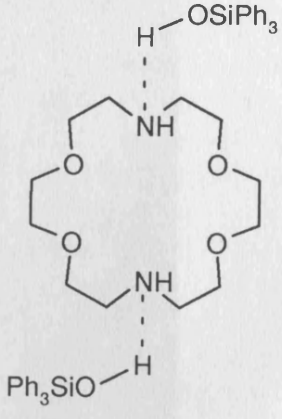

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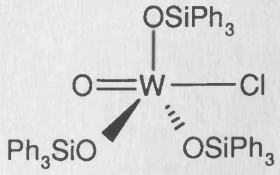

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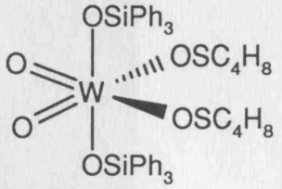

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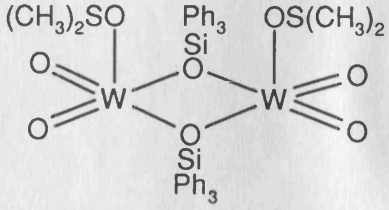

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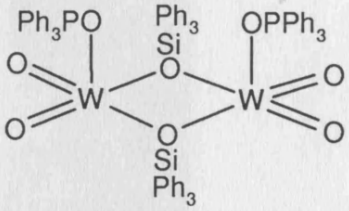

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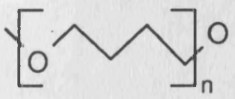

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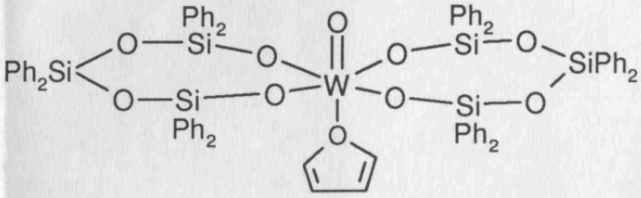

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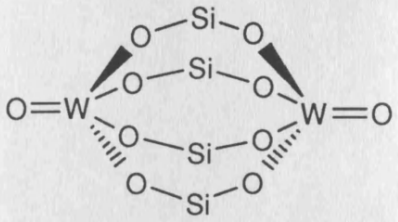

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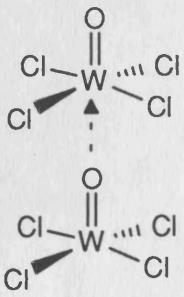

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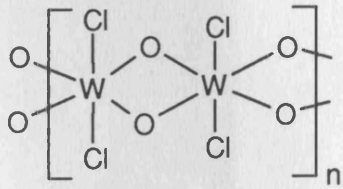

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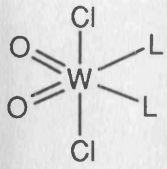
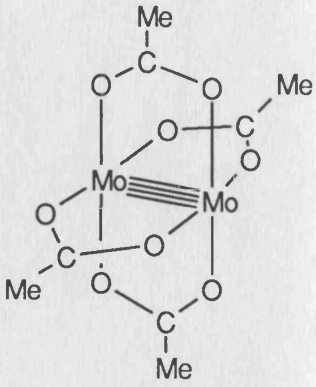


L = DMSO (**M3**)
= TMSO (**M4**)
= Ph_3PO (**M5**)



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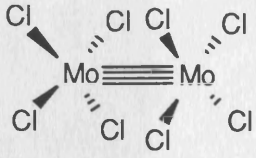

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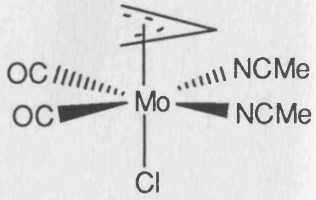

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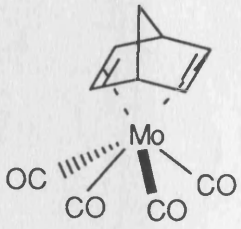
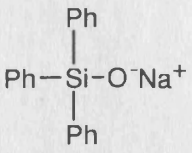


(**M9**)

Schematic Diagrams of the Compounds Prepared



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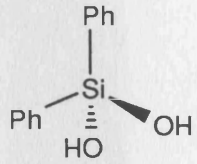

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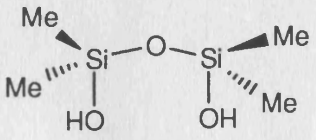

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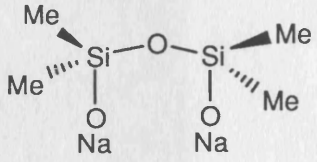

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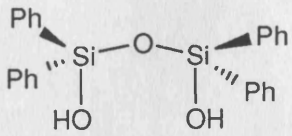

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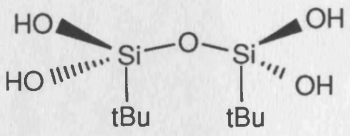

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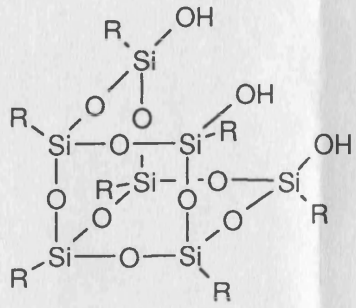

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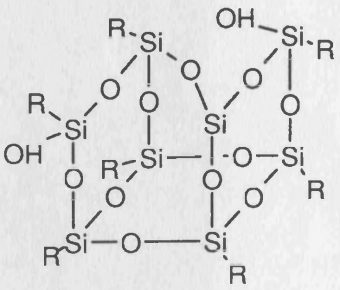
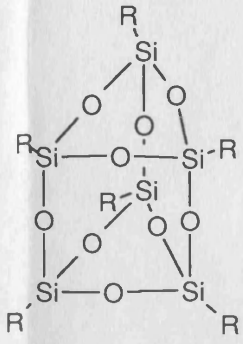


(**S9**)



(**S4**)

Preface

"Catalysis - the chemical influence of a substance which is not itself permanently changed"

Chambers English Dictionary

"Current state-of-the-art techniques are still not amenable to detailed mechanistic studies of silica supported species, and there is considerable debate as to the nature of the active species involved in catalysis. In contrast, homogeneous systems are more easily studied and the chemistry of homogeneous catalysts is easier to delineate. The development of useful homogeneous models for heterogenous catalysts therefore offers an opportunity to develop a molecular understanding of heterogeneous catalysts which could lead to better strategies for control of selectivity, activity and catalyst lifetime"

F.J. Feher and T.A. Budzichowski

Polyhedron, **14**, 3239 (1995)

Chapter One: Introduction

1.1 OVERVIEW

The origins of many of the synthetic materials and fibres we take for granted today lie in the catalysed conversion of organic feedstocks obtained from the petroleum and natural gas industries. In particular small hydrocarbons such as methane, ethylene, propylene and butadiene are transformed in bulk quantities into oxygenated compounds such as alcohols, ketones, carboxylic acids or polymerised to higher olefins, *e.g.* polyethylene, polypropylene or rubbers. These materials, the "building blocks", form the starting point for many of the modern organic derivatives found throughout industry.

Whilst catalysts revolutionised industrial chemistry in the early 1900s, even today it is difficult to overstate their scope and importance in contemporary technology, a fact born out by the abundance of attendant literature. Nevertheless, our attempts to quantify materials displaying the requisite properties may be broadly divided into two catagories. The first, that of species involved in the heterogeneous catalysis of reactions, *e.g* a gas being passed over a solid substrate that evidently undergoes no change, essentially represent the truest meaning of the phrase. However, homogeneous reactions are altogether more ambiguous as the catalytic cycle is more likely to proceed *via* a series of linked chemical reactions with more than a single species participating. Thus, in this context, the notion of a particular species being the "catalyst" has no real validity.

Industrially, heterogeneous processes offer greater practical advantages over homogeneous catalysis, due to the ease of separating the products from any excess of reactants and catalyst. However, a number of homogeneous catalysts have been developed that offer greater selectivity of reaction and operate under milder reaction conditions than heterogenous catalysts. Processes occurring in solution also present the opportunity to study mechanistically and spectroscopically the reaction cycles through characterisation, and in certain cases isolation, of the reaction intermediates. As a result mechanistic insights into heterogeneous reactions are often obtained through applying the principles learned from the study of the latter reactions.

In most conversions starting from methane or petroleum fractions, transition metals or their compounds are used as catalysts, heterogeneously on oxide, carbon, silica or alumina supports, or where necessary in order to obtain greater selectivity, in homogeneous solution. Whilst it is the metal centre that determines the reactivity and selectivity of the reaction(s), the role of the supporting substrate is crucial in determining the key factors of steric and electronic (un)saturation of the reactive moiety. This enables a second approach to be employed in elucidating hetero- and homogeneous processes.

Synthesis of metal centres with appended ligand sets displaying similar properties to the supporting substrate allow detailed structural and reactivity studies to be undertaken. In the case of oxophilic, high oxidation state species used in large scale olefin polymerisations and Fischer-Tropsch carbonylations, the metal centres are often supported on a silica surface, or in model compounds by an organosiloxide analogue.

Until recently the chemistry and structural characteristics of silanols remained relatively ill-defined despite their widespread use as both precursors in polysiloxane formation and as potential models for silica surfaces. The paucity of literature in this structurally demanding arena has only begun to be redressed by progressions in synthetic methodology and the ready availability of advanced analytical tools. Thus the first section of this thesis is devoted to the vast wealth of information concerning the preparation, properties and structural studies of silanol compounds. In particular, attention is given to those which display interesting structural features or act as potential models for silica substrates. The subsequent section highlights the changes in structural and electronic properties, as well as reactivity patterns, when a catalytically active metal centre is appended to a model ligand set.

Whilst siloxides function as excellent supporting ligands for high oxidation state, oxophilic metal centres used in olefin polymerisations, allylic and alkenic metathesis reactions are also catalysed homogeneously by low oxidation state early transition metals. These moieties are stabilised and supported by softer, π-donor interactions, therefore the last section is devoted to interactions of metals in low oxdiation states supported by oxo- and aza-crown ethers.

1.2 SILANOLS AND SILOXANES

1.2.1 INTRODUCTION

The history of silicon and its related compounds was initially, and is to some extent even today, overshadowed by attempts to associate its chemistry with that of its fellow group 14 elements. When silicon was first isolated along with its tetrachloride ($SiCl_4$) by J.J. Berzelius in 1823 it was expected to mirror the vast wealth of covalent chemistry of carbon and its organic compounds. Continual failures in attempts to produce silicon analogues of carbon may have been in hindsight better understood by a comparison of the electronic properties of the silicon atom with those of its congeners. Thus perusal of table 1 reveals the enormous discontinuity between the first- and second row elements and thereafter highlights the gradual change as metallic character increases from the metalloid germanium through to lead. It is not surprising then that perhaps nowhere else in the periodic table does the chemistry of an element show such notable discrepancies with that of the others within its group.

Atomic Properties	Carbon (C)	Silicon (Si)	Germanium (Ge)	Tin (Sn)	Lead (Pb)
Electronic configuration	$[He]2s^2 2p^2$	$[Ne]3s^2 3p^2$	$[Ar]3d^{10}4s^2 4p^2$	$[Kr]4d^{10} 5s^2 5p^2$	$[Xe]4f^{14} 5d^{10}6s^2 6p^2$
Atomic radius	73 pm	118 pm	123 pm	141 pm	175 pm
Covalent radius	77 pm	117 pm	122 pm	140[a] pm	146 pm
Effective nuclear charge (Clementi)	3.14	4.29	6.78	N/A	N/A
Electronegativity (Pauling)	2.5	1.8	1.8	1.8	1.9

[a]Covalent radius of Sn^{II} 163 pm

Table 1 The atomic properties of carbon and silicon

Accordingly the drive to produce the first silicon analogues of carbon chemistry was hindered by the relative weakness of the Si-Si (226 kJ mol^{-1}) bond in comparison (table 2) with that of the C-C bond (348 kJ mol^{-1}) and means that Si-Si containing polymers are comparatively unstable. As a result interest in the area subsided until in the 1860s Friedel, Crafts and Ladenburg synthesised the first organosilane, tetraethylsilane. In the immediate aftermath the isolation and characterisation of many reactive organochlorosilanes were reported. Hydrolysis of these precursors produced polymers in which the primary chain was composed of alternating atoms of silicon and oxygen framed by organic groups. These polymers opened new vistas in chemistry. They did not copy natural substances (no such compounds exist in nature) and they were thus a laboratory development from start to finish. The first of this new group of compounds known as polyorganosiloxanes or silicones were reported by a Russian group in 1937 and revolutionised the field of polymer chemistry.[1]

Silicon Bond	Bond energy kJ/mol	% Ionic character	Carbon Bond	Bond energy kJ/mol	% Ionic character
Si-Si	226	-	**C-Si**	301	12
Si-C	302	12	**C-C**	348	-
Si-H	326	3	**C-H**	339	4
Si-O	485	51	**C-O**	355	22
Si-N	355	30	**C-N**	304	7
Si-F	582	70	**C-F**	484	43
Si-Cl	391	30	**C-Cl**	338	7
Si-Br	309	22	**C-Br**	284	3
Si-I	234	12	**C-I**	213	0
Si=Si	318	-	**C=C**	610	-

Table 2 Average bond energies and calculated ionic character of selected silicon and carbon bonds

The exceptional importance of synthetic macromolecular compounds brought about by the start of World War II focused intensive research efforts on the synthesis and characterisation of silicones. Their greater thermal and thermoxidative stability in comparison to many of the common organic polymers was coupled with good electrical and mechanical properties, low surface energy, hydrophobicity, film forming ability, high permeability to gases, biocompatability and chemical and photochemical inertness which rendered them useful in many applications. The high thermal and thermoxidative stability of polyorganosiloxane polymers can be attributed to the strong, partially ionic, Si-O linkage and the strength of the Si-C bond of the appended functional groups (table 2). Disposition of other technically valuable assets, such as the temperature resistance (both high and low) and mechanical properties (viscosity, compressibility, modulus of elasticity and flexibility) is achieved by reconciling the nature of the pendant groups with the degree of cross linking allowed within the polymer.

Commercially, control over the conditions under which hydrolysis is undertaken have changed relatively little since they were first manufactured in 1943. However the search to optimise processes resulted in the identification of conditions necessary for the isolation and characterisation of some only partially hydrolysed intermediates consisting of monomeric and oligomeric compounds. In the laboratory Ladenburg[2] had already prepared the first of these compounds, Et_3SiOH, initially christened "silicoles" in 1871 through the hydrolysis of Et_3SiCl with aqueous ammonia, but their importance in industrially relevant chemistry had now been revealed. Greater understanding of their chemistry and changes in nomenclature now categorise these compounds as organosilanols and they can be thought of in many ways as formal analogues of alcohols, despite their very different reactivity patterns. An excellent up-to-date review of the relevant literature has been prepared by Lickiss.[3]

1.2.2 PREPARATION OF SILANOLS AND SILOXANES

Monomeric functionalised organosilanols may be prepared by a wide variety of synthetic methods, however the simplest, most economical, and most frequently used route involves the hydrolytic process. Fundamental hydrolysis processes involve the cleavage by water, of a functional group appended to the silicon atom, and they can be most easily achieved when the functional group (X) has a high electronegativity. The resulting highly polarised Si-X bond renders the silicon centre susceptible to nucleophilic attack. Thus compounds in which the silicon carries one or more halogen, OR, OCOR, NH_2, HNK, SR, or OSO_3H, groups are hydrolysed with particular ease. In many cases the rapid rate at which organosilanes hydrolyse has rendered the study of reaction mechanisms difficult. It is believed that many proceed *via* a 5-coordinate transition state with the reactions kinetics

being affected by the electronic properties of the substituents appended to the silicon centre, and of the leaving group.

Hydrolysis reactions lead initially to the formation of unstable silanols, which in the presence of trace amounts of base, acid or heat can readily eliminate water to form stable siloxanes. These self- or polycondensation reactions are useful in producing long chain or cross-linked polymers as well as cyclic siloxanes, but they represent a serious practical problem in the targeting of mono- and oligomeric silanol species. Consequently attempts to synthesise and isolate silanols should heed the following practical points

(i) The bimolecular (in silanol) nature of condensation reactions means the use of dilute solutions will be advantageous. Solvents such as Et_2O/$^tBu_2O$ and toluene are commonly utilised as they are either immiscible or only slightly miscible with water and also demonstrate no reactivity to the silanol precursor. These solvents also confer useful product distribution and separation properties since the hydrolysis products are extracted by the solvent and are thus protected from further aqueous acid/base attack.

(ii) Systems in which an acid or base is generated should be avoided if possible. If such products are formed they should be immediately neutralised. For example in the hydrolysis of a chlorosilane, which generates HCl, an amine can be utilised to adjust the pH and prevent acid catalysed condensation.

(iii) Hydrolysis reactions are exothermic and thus reactions should be carried out slowly at the lowest convenient temperature.

(iv) The number of non-hydrolysible functional groups and their nature determines the tendency for silanol versus siloxane formation. The use of one or more bulky, *i.e.* ^{t}Bu or $(CH_3Si)_3C$, groups will reduce significantly the proclivity for siloxane formation on hydrolysis, and may prevent even silanol formation.

A. HYDROLYSIS OF HALOSILANES

Because of their readily available nature alkyl- (or aryl-) halosilanes (especially chlorosilanes) are the starting materials most widely used in hydrolytic reactions. When water reacts with the halosilane, the silicon-halogen bond is cleaved and the unstable intermediate hydrolysis products such as trialkyl- (or aryl-) silanols, dialkyl- (or aryl-) silanediols and alkyl- (aryl-) silanetriols are formed. If the correct conditions are utilised these may be isolated as monomers. The reactions can be represented as:

$$R_3SiX + H_2O \rightarrow R_3SiOH + HX$$

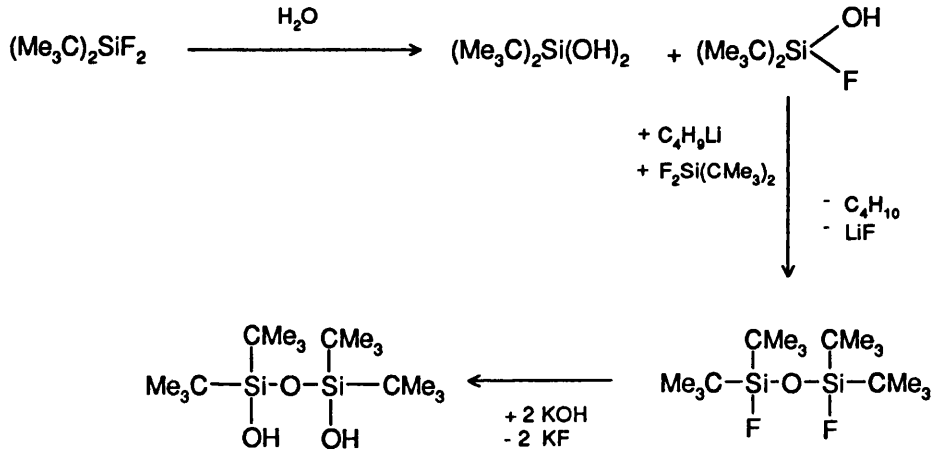
$$R_2SiX_2 + H_2O \rightarrow R_2Si(OH)_2 + 2HX$$

$$RSiX_3 + H_2O \rightarrow RSi(OH)_3 + 3HX$$

Unless adequately neutralised the HX generated will lead to the formation of disiloxanes in the first reaction, linear and cyclic siloxanes in the second, and a mixture of branched and cross-linked siloxanes in the third.

(i) Fluorosilanes

Silyl fluorides containing one or more sterically demanding functions, *i.e.* ^{i}Pr or ^{t}Bu, are hydrolysed under alkaline conditions to give the corresponding silanols and silanediols in moderate to high yields. Fluoro- silanes and silanols can serve as useful starting materials for the stepwise construction of chain siloxanes containing the highly hindered *tert*-butyl groups (scheme 1).



Scheme 1 The synthesis of hexa-*tert*-butyldihydroxydisiloxane

Although the third step in the process is not hydrolytic, this reaction has been developed as a route to a number of sterically demanding linear silanols, which after further condensations produce cyclosiloxane species.[4]

(ii) Chlorosilanes

The ready availability and high reactivity of chlorosilanes means they are by far the most commonly utilised in hydrolysis reactions, with precautions taken to neutralise the HCl liberated. As can be seen from table 3 the difficulty of isolating partially hydrolysed products is related to the number and bulk of the organic substituents.

Chlorosilane	Process conditions	Major isolable products	Ref
Me_3SiCl	H_2O/C_6H_6	$Me_3SiOSiMe_3$	5
	H_2O/NaOH	Me_3SiOH	6
$^tBu_3SiCl$	EtOH/KOH reflux 2 days	$^tBu_3SiOH$	7
Ph_3SiCl	$H_2O/(NH_4)_2CO_3/C_7H_8$	Ph_3SiOH	8
Me_2SiCl_2	H_2O	cyclic $(Me_2SiO)_n$ + $HOMe_2Si(OSiMe_2)_nH$	
	$(NH_4)_2CO_3/H_2O$, low temperature	$Me_2Si(OH)_2$ + $(HOMe_2Si)_2O$ + $HO(SiMe_2O)_nH$ n = 3-5	9
$^tBu_2SiCl_2$	MeOH/KOH/Et_2O	$^tBu_2Si(OH)_2$	10
Ph_2SiCl_2	$(NH_4)_2CO_3/H_2O/Et_2O$	$Ph_2Si(OH)_2$ + $HO(SiPh_2O)_nH$ n = 2, 3 + $(Ph_2SiO)_n$ n = 3, 4	9 11
$MeSiCl_3$	H_2O - under any conditions	$(CH_3SiO_{1.5})_x$	12
$^tBuSiCl_3$	$H_2O/PhNH_2/Et_2O$	$^tBuSi(OH)_3$	13
	MeOH/KOH/Et_2O low temperature	$(^tBu(OH)_2Si)_2O$	14
$(c\text{-}C_6H_{11})SiCl_3$	$H_2O/PhNH_2/Et_2O$	$(c\text{-}C_6H_{11})_3Si(OH)_3$	15
	$(CH_3)_2CO/H_2O$	Cage compounds shown below	16
	3+ months		11b
$PhSiCl_3$	$H_2O/PhNH_2/Et_2O$	$PhSi(OH)_3$	17

Table 3 The hydrolysis of common chlorosilanes

Small alkyl ligands such as methyl, and to a lesser extent ethyl functions, offer little in the way of bulk and so their silanols readily undergo condensation reactions unless very careful control over conditions is exercised. To date the compound $MeSi(OH)_3$ has yet to be isolated as it spontaneously condenses in all media under acidic, basic or neutral conditions. Phenylsilanol compounds, containing one, two or three hydroxy functions may be produced and isolated under comparatively mild conditions whilst strongly basic conditions are required to hydrolyse *tert*-butyl silicon chlorides. The severe conditions required to hydrolyse these precursors are tempered by the stability of the silanols. Their extreme resistance to form siloxanes through condensation reactions is epitomised by $^tBu_2Si(OH)_2$, which is reported to remain intact unless refluxed in heptane with *p*-toluenesulphonic acid.[18] Exceptionally large substituents, *e.g.* $(Me_3Si)_3C$, are particularly resistant to hydrolysis with even the formation of $(Me_3Si)_3CSi(OH)_3$ from its trichloride proving difficult.[19]

As discussed previously the composition and properties of the hydrolysis products depend to a considerable extent on the reaction conditions, such as reactant stoichiometry, acidity of the medium, the presence (or absence) of a solvent and its polarity. Thus the hydrolysis of Ph_2SiCl_2 to yield a mixture of diphenylsilanediol, α,ω-dihydroxypoly(diphenylsiloxanes), hexaphenylcyclotri- and octaphenylcyclotetrasiloxane is paradigmatic of these symptoms. This reaction is performed under dilute

conditions in a homogeneous medium, normally diethyl ether, which provides reasonable reactant solubility allied with good product partitioning. The neutrality of the solution is maintained by using a weak base, often ammonium carbonate, to neutralise the HCl formed *in situ* which ensures that the cyclisation of products is minimised. The initial hydrolysis products formed are $Ph_2Si(OH)_2$ and α,ω-dichloropoly(diphenylsiloxanes) which may be isolated if required. Further hydrolyses to dihydroxypoly(diphenylsiloxanes) occurs upon prolonged reflux. Specific hydrolysis products may be targeted by varying the initial reactant stoichiometries. Thus a water:diphenyldichlorosilane ratio of 1:1.5 gives a higher yield of dihydroxyhexaphenyltrisiloxane and less dihydroxytetraphenyldisiloxane whilst a reduction in the molar ratio to 1:1 or 1:0.67, results in the formation of hexaphenylcyclotrisiloxane almost exclusively.

Rates of hydrolysis not only produce different product ratios but also lead to widely different products. Carefully controlled hydrolysis of $RSiCl_3$ (R = ^{t}Bu, Cp, *c*-C_6H_{11}) leads to the formation and isolation of the unstable silanols $RSi(OH)_3$ which may readily undergo self condensation reactions. In contrast, slow hydrolysis in aqueous systems where no pH control is exerted, produces partially and completely hydrolysed cage compounds.[20]

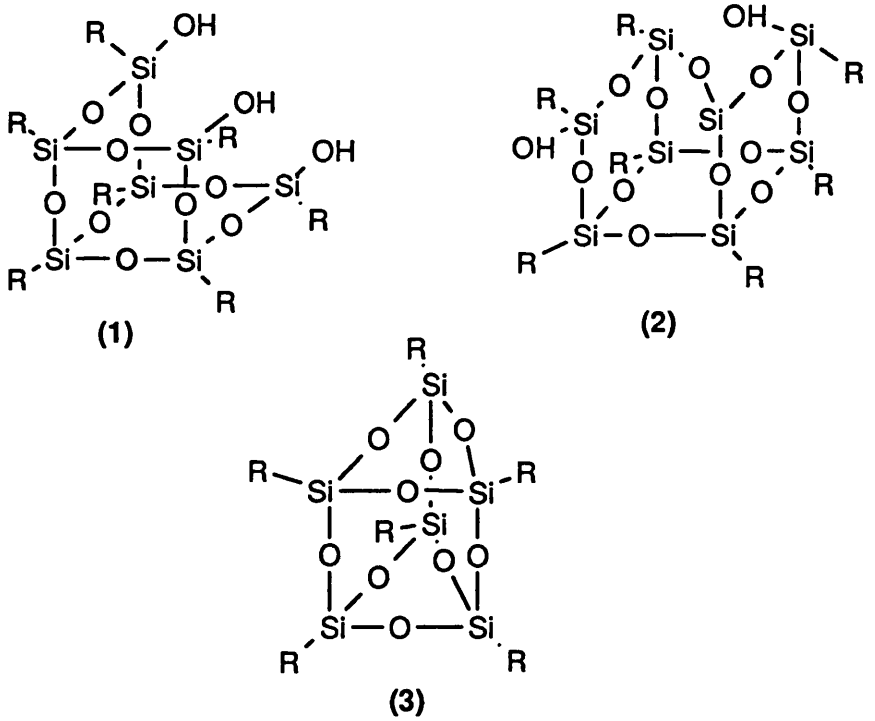


Figure 1 Condensed silesquioxanes from hydrolysed $RSiCl_3$

Interest has centred particularly on the cyclohexyl derivative $CySiCl_3$ which gestates in acetone/water over a period of several months/1 year to yield a mixture of three products, two of which are incompletely condensed silesquioxanes (**1**) and (**2**). The final product is the completely condensed siloxane cage structure (**3**) (figure 1). Trisilanol (**1**) is widely accepted as the best available model of the surfaces of silica.[21] Of particular significance are the short-range structural similarities between

(1) and geometrically comparable trisilanol sites available on idealised surfaces of β-cristobalite (111) and β-tridymite (0001), two SiO_2 polymorphs that have been frequently suggested to resemble amorphous silica surfaces.

In the absence of a base, metal cluster compounds may be utilised to control the hydrolysis and prevent condensation even during exposure to acidic media.[22]

$$Me_nCl_{3-n}SiCCo(CO)_9 \xrightarrow[\text{reflux 30 min}]{C_6H_6 / H_2O} Me(OH)_{3-n}SiCCo_3(CO)_9 \qquad \textbf{1.1}$$

Silyl chlorides may be hydrolysed under aqueous base conditions to produce transition metal-silanol species, such as $[WCp^*(CO)_2(PMe_3)\{SiMeH(OH)\}]$[23] which demonstrates appreciable stability due to the reduced acidity of the silanol function caused by the electron donating nature of the metal fragment. Bulkier ligands attached to the silicon centre may allow direct reaction with a metal moiety to form a metallosilanol.[24]

(iv) Bromo and Iodosilanes

Silyl bromides are rarely used as starting materials for silanol synthesis although cleavage of the Si-Br bond is achieved in a manner similar to that of chlorosilanes. Hydrolysis of bromosilanes containing silicon centres with sterically demanding functions often requires harsh conditions and offers no guarantee of success !

$$\{(Me_3Si)_3C\}SiBr_3 \xrightarrow[\text{72 hrs reflux}]{\text{1\% v/v } H_2O/EtOH} \{(Me_3Si)_3C\}SiBr_3 \qquad \textbf{1.2}$$

However organo(bromo)silanes containing less sterically demanding substituents react readily with water to give 1,3-diorganodisiloxanes and HBr. Reactions on small scales[25] are relatively unaffected by the presence of the acid but on scaling up the yield is considerably improved by the presence of $CaCO_3$ as an acid scavenger.[26]

Whilst rates of hydrolysis of iodosilanes are slower than those for either chloro- or bromo-silanes, they react more readily than fluorosilanes or silanehydrides. The presence of bulky substituents, as in all halosilanes, inhibits the rate of reaction and vigorous reaction conditions over prolonged timescales are often employed to ensure that acceptable yields of product can be isolated.

$$(Me_3Si)_3CSiMe_2I + 2\%H_2O \xrightarrow[\text{or}\ \text{(ii) DMSO 130 °C 1 hr}]{\text{(i) Aq dioxane 1 hr reflux}} (Me_3Si)_3CSiMe_2(OH) + HI \qquad \textbf{1.3}$$

Access to hindered silanols *via* this route is greatly assisted by the addition of silver salts in aqueous media. This enables the ready formation of silanols *via* hydrolysis of the iodosilane and/or a bridging silicocation intermediate species.[27] Iodosilanes with severely sterically demanding substituents, are readily hydrolysed to the corresponding silanol in the presence of metachloroperbenzoic acid (mcpba). These systems exhibit rates far exceeding those in the hydrolysis of the corresponding fluoro- and organosilanehydrides. The higher reactivity is attributed to the formation of a more stable leaving group, IO_n, through oxidation of the iodide ligand.[28]

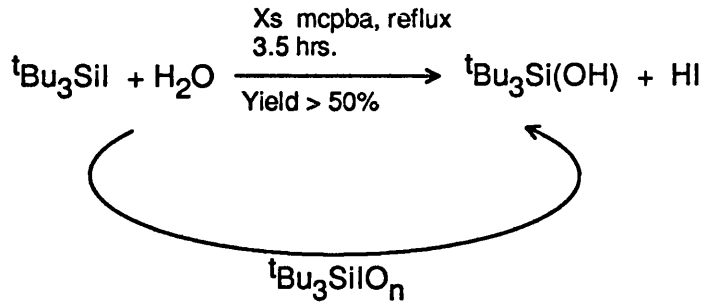


Figure 2 Hydrolysis of iodosilanes

B. HYDROLYSIS OF OTHER FUNCTIONAL GROUPS

(i) Si-O functions

A large body of literature exists detailing the hydrolysis of alkoxysilanes, which are widely employed within industry as coupling agents to attach metal moieties or organo functional groups to silica substrates. Rates at which the hydrolysis of alkoxysilanes occurs is dependent upon the pH of the solution with the slowest rates occurring under neutral conditions, and the rate increasing by a factor of about 10 per increment of pH. Careful hydrolysis is an extremely useful method for preparing very sensitive silanols containing small substituents, as the alcohol formed as a by-product (*cf.* halosilanes) is less likely to encourage self-polymerisation reactions.[8]

$$Me_2Si(OEt)_2 + H_2O \xrightarrow[24\ hrs\ RT]{CaCO_3} Me_2Si(OH)_2 + EtOH \qquad \textbf{1.4}$$

If the substituents are large enough to prevent condensation, hydrolysis may be performed in acidic media. Thus $[(c\text{-}C_6H_{11})_3SiO(c\text{-}C_6H_{11})]$ is hydrolysed to its silanol in hot concentrated acid.[29] Good yields of α,ω-diols are obtained by the hydrolysis of α,ω-acetoxy compounds using a base (nominally $CaCO_3$) to neutralise AcOH formed *in situ*.[30]

$$Ac(SiRR'O)_nAc + H_2O \longrightarrow HO(SiRR'O)_nH + AcOH$$

$$n = 2\text{-}6 \text{ for } R = R' = Me;\ n = 2\text{-}4 \text{ for } R = Me,\ R' = CF_3CH_2CH_2 \qquad \textbf{1.5}$$

Cleavage of Si-O bonds leading to ring opening reactions occurs upon treatment of cyclosiloxanes with alkyl or aryl lithium reagents.[31] The reactions are highly specific to the solvent/lithium reagent employed, with experiments indicating that silanols can be isolated in good yields using BuLi reagents in toluene/ether solutions, followed by an aqueous work up.[32]

$$(Ph_2SiO)_3 + 3.3\ RLi \xrightarrow[(ii)\ H_3O^+\ workup]{(i)\ reflux} 3\ Ph_2RSiOH$$

$R = Me, {}^{n}Bu, {}^{s}Bu$ or ${}^{t}Bu$ **1.6**

(ii) Triflates, perchlorates, cyanates, sulphates and other functions

A wide variety of substituents bonded to silicon centres act as good leaving groups and thus provide easy access to silanols. Silyl triflates, perchlorates and cyanates are all readily hydrolysed, even in sterically crowded molecules, however the formation of H_2SO_4 during the hydrolysis of silyl sulphates tends to preclude their use in practice.

$$(Me_3Si)_3CSiMe_2OSO_2CF_3 \xrightarrow[1\%\ H_2O]{MeOH} (Me_3Si)_3CSiMe_2(OH) + TrifOH$$ **1.7**

Compounds containing Si-N functions can usually be hydrolysed but precautions similar to those used in the hydrolysis of halosilanes must be undertaken. Thus dilute hydrochloric acid is used to buffer and maintain the neutrality of the solution during the hydrolysis of $(Me_3Si)_2NH$.[5]

$$(Me_3Si)_2NH + H_2O \xrightarrow[(ii)\ 2M\ HCl]{(i)\ Et_2O} Me_3Si(OH) + 2\ NH_3$$ **1.8**

Alkyl or aryl functions which can act as a suitable leaving group can be used to prepare silanols by the cleavage of an Si-C bond. Good carbon centred leaving groups can lead to competition between scission of the Si-C bond and that of Si-X. Thus under acidic, basic or neutral conditions Ph_2SiCl_2 forms $Si(OH)_4$ and not the expected $Ph_2Si(OH)_2$.[33] However under more moderate conditions, reaction with moist ether for a short time followed by immediate separation of the products, the expected diol is isolated.

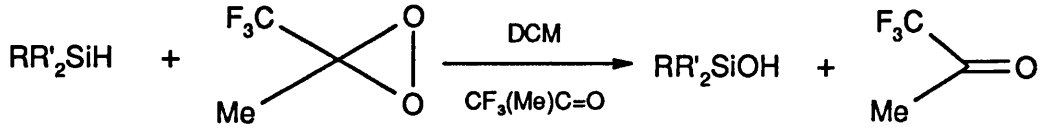
There is a relative paucity of published information concerning the hydrolysis of Si-M (M = metal) functions. As the author can testify this discrepancy is almost certainly due to the unwitting nature of the reactions caused by the decomposition of the target molecules. Bonds may be cleaved in a more deliberate manner, with $[Ti(SiPh_3)_4]$ reported to form Ph_3SiOH *via* a Ph_3SiH intermediate during alkaline hydrolysis.[34]

C. FROM Si-H COMPOUNDS

(i) Oxidation

Organosilanes containing small organic functions (R = Me, Et, ^{n}Bu) together with several Si-H bonds are highly reactive and can ignite in contact with oxygen in the presence of a metal. Silanes with larger substituents or a reduced number of Si-H bonds prove more stable and may be isolated by distillation. The use of oxidising agents such as perbenzoic acid,[35] the silver salts $AgNO_3$, $AgNO_2$, AgO[36] as well as HgO[37] are all reported to give silanols in good yields in low boiling solvents. The more powerful oxidant, $KMnO_4$, often used in conjunction with ultrasound to aid its solubility in organic solvents, produces good yields of silanol in sterically hindered systems.[3]

Rapid oxidation of organosilanes at low temperatures may be achieved by ozonolysis, but large organic subsituents, *e.g.* ^{t}Bu, are required to prevent siloxane formation.[38] Dioxiranes can be utilised in the formation of sensitive silanol compounds where low temperature and the absence of base or acid is essential.



1.9

This powerful synthetic tool oxidises Et_3SiH to Et_3SiOH in less than one minute[39] at temperatures ranging from -20 to 0°C and will also oxidise Si-H functions within a transition metal sphere. Thus $[WCp^*(CO)_2(PMe_3)SiRH_2]$ reacts with dioxirane reagents to form $[WCp^*(CO)_2(PMe_3)\{SiR(OH)_2\}]$ (R = Me/OH).[23a]

(ii) Hydrolysis

Organosilanes (R = alkyl, phenyl, napthyl) react slowly if at all with water but the rate of hydrolysis is rapidly increased in the presence of acid or especially base. These reactions are synthetically poor if attempts are made to isolate silanols containing small organic groups where reaction conditions favour condensation of the intermediates. Silanol species containing bulkier substituents may be isolated. Milder conditions, for example a buffered, aqueous solution at room temperature or just above, is employed in transition metal catalysed hydrolyses. Rhenium, platinum and rhodium supported on charcoal or alumina substrates all produce good yields of silanol, although the best results are usually obtained with palladium catalysts.[40]

1.2.3 CHARACTERISATION

A. INFRARED SPECTROSCOPY

Silicon compounds give rise to characteristic infrared absorption frequencies which are normally appreciably more intense than those arising from carbon. This fact is of considerable help in analytical work, and infra-red absorption spectra are extensively deployed in the development and characterisation of organo-silicon polymers and related materials. A review of available data is not possible in this space, and the reader is directed to several review articles[41] as well as the selected tabulated data below.

Function	Wavenumber (cm^{-1})
Si-H: stretch	2300-2100 m-s
deformation	950-890 m
Si-C stretch	900-700s
Si-$(CH_3)_3$	~1250, 840, 763 s
Si-$(CH_3)_2$	~1259, 855, 800 s
Si-(CH_3)	~1259, 763 s
Si-(C_6H_5)	1429, 1130-1090 s
Si-O-Si stretch	
cyclic- trimers	1020-1010 s
tetramers	1090-1080 s
higher rings	1080-1050 s
open chains	1100-1000 s
SiO-H def	890-820 s
SiO-H stretch	3700-3300 b
SiO-M	1000-910 s

Table 4 Selected IR data for silanol compounds

(i) Silicon-Carbon Vibrations

The stretching vibration of the Si-C linkage occurs in the 900-700 cm^{-1} region of the spectrum with the exact positions determined by the nature of the substituent groupings. In linear methylsiloxane polymers the Si-C stretching band occurs at around 800 cm^{-1} (~814-803 cm^{-1} for cyclosiloxanes) whilst characteristic rocking bands of the end $Si(CH_3)_n$ appear at around 840 cm^{-1} and decrease in intensity with the length of the chain (in cyclosiloxanes this band is absent). Deformation vibrations of methyl groupings attached to the silicon are generally found between 1265 and 1250 cm^{-1}. Characteristic bands due to silicon-phenyl linkages have been assigned around 1430 and 1110 cm^{-1} whilst

normal mono-substituted aromatic ring vibrations at 740-735 cm^{-1} appear to be substantially unaffected.

(ii) Silicon-Oxygen Vibrations

Almost all siloxane compounds show at least one strong band in the region, 1100-1000 cm^{-1} arising from the Si-O-Si asymmetric vibration. The position of the band is dependent upon the substituents appended to the silicon centre and in siloxanes the length of the polymer chain. Thus in disiloxanes the band occurs between 1124-1020 cm^{-1} but in long chain siloxanes the band splits into two with maxima at around 1087 and 1020 cm^{-1}. The shift to a lower wavenumber of the Si-O band in small cyclosiloxane systems, *i.e.* hexaphenylcyclotrisiloxane (1020-1010 cm^{-1} *cf.* 1093-1081 cm^{-1} for the cyclic tetramer), has been attributed to the greater ring strain for the planar structure in comparison to the larger non-planar rings. Silanols show strong concentration dependent absorptions due to SiO-H stretching between 3700-3300 cm^{-1}. In dilute solution the free SiO-H stretching mode is found around 3680 cm^{-1} whilst the bonded OH groups appear at around 3300 cm^{-1} (see also section 1.2.5). SiO-H groups also exhibit asymmetric Si-O stretching absorptions in the range 910-830 cm^{-1}. Metal derivatives of silanols typically give rise to SiO-M stretching absorptions in the range 1000-910 cm^{-1}.

B. ^{29}Si NMR SPECTROSCOPY

Silicon has only one naturally occurring NMR active isotope, that of ^{29}Si, I=1/2, which is found only in low abundance. Coupled with the low sensitivity of the nucleus and its relatively long relaxation times, this has in the past rendered its study uncommon in comparison with that of other nuclei. However the advent of new pulsed and decoupled techniques made available by modern FT spectrometers has realised a rich vein of investigative chemistry. This section conveys only the briefest overview of silicon NMR and relates mainly to matters which concern the practical accumulation and manipulation of spectra. The reader is directed to one of any excellent treatises on inorganic and silicon NMR should they wish to pursue the subject in detail.[42]

Despite the relative ease with which silicon NMR spectra may now be acquired, practical considerations remain dominated by the nuclear Overhauser effect (NOE) and long spin relaxation times.

(i) Nuclear Overhauser Effect (NOE)

In obtaining proton decoupled ^{29}Si spectra the effects arising from the dipole-dipole relaxation mechanisms predominate leading to a NOE which is strongly negative (-1.5). As a result a decrease in signal to noise (S/N) ratio is observed, or in some instances expected resonances may not be observed at all. The NOE may be overcome by using pulse modulated (commonly referred to as gated)

decoupling techniques. These have the advantage of being non-reliant on paramagnetic shift reagents which may exert some change in chemical shift. However, this is problematic in that the long recovery times between pulses leads to an inefficient build up of signal, but despite the enhanced effect the T_1 remains the same (*vide infra*) and so realises useful signal intensities.

(ii) Relaxation Effects

The observation of an NMR signal is connected with the absorption of radio frequency quanta which promote some nuclear spins to a higher spin state. In the case of silicon, I = 1/2, there is only one level. This absorption however perturbs the thermal equilibrium that exists between the spin states and is eventually dissipated to the surroundings (lattice) to restore equilibrium. This process is known as spin-lattice relaxation, T_1, and is defined as the time in which the excess spins of higher energy are reduced by a factor of e = 2.718.

There are several mechanisms which contribute to the exchange of energy between the spin system and its surroundings with the rates of these processes being additive.

- nuclear magnetic moment
- chemical shift anisotropy
- spin rotation interaction
- scalar relaxation
- electronic interactions

At room temperature and above the spin-rotation interaction is the dominant relaxation mechanism. However T_1 can be considerably reduced by the addition of only a small amount of shiftless paramagnetic reagent, chromium(III)acetylacetone, $[Cr(acac)_3]$, being the most widely used. The high magnetic moment associated with this paramagnetic complex, present in approximately 10^{-2} M in solution, reduces T_1 to less than 10 seconds and renders relaxation independent of all other sources. This effect also results in the suppression of the NOE, and hence line intensities in the ^{29}Si spectrum become proportional to the their concentration providing there is ***no*** complexation between the chromium complex and the silicon species.

(iii) Chemical Shifts

^{29}Si NMR chemical shifts occur within a range of 500 ppm although most lie within a narrower band of 120 ppm, and as with other NMR active heavy atoms (^{15}N, ^{19}F, ^{31}P, ^{119}Sn), resonances of many classes occur in overlapping regions. Shifts are generally measured relative to tetramethylsilane (TMS, also used in ^1H and ^{13}C NMR) which displays low reactivity and only very minor shifts due to variations in concentration. Spectra are generally recorded in high concentration or saturated so-

lutions in order to minimise shift changes caused by differences in concentration. Compounds containing all or mainly covalent bonds, *i.e.* TMS, display only small concentration dependent changes in chemical shift. However the introduction of polar groups, *i.e.* silanols, results in greater dipole moments and so the shift becomes dependent upon concentration and the electron pair donating ability of the solvent (table 5). Hence good donor solvents result in shifts to lower fields .[43]

Compound	$CHCl_3$	Acetone	DMF
Ph_3SiOH	-12.6	-16.2	-17.5
$Ph_2Si(OH)_2$	-30.7	-32.4	-34.2
$(HOMe_2Si)_2O$	-10.5	-13.6	-14.9

Table 5 Effect of solvent on the ^{29}Si chemical shift of silanols and siloxanes

^{29}Si NMR chemical shifts are now well understood theoretically, with the following influences being empirically demonstrated *viz.*

- substituent electronegativity
- steric interactions
- variations from tetrahedral arrangement around silicon
- co-ordination number at silicon
- π-bonding involving silicon

The high sensitivity of the ^{29}Si nucleus to its local environment enables a great deal of structural information to be inferred from chemical shift data. For Si-O compounds, the shift is strongly dependent upon the number of oxygen atoms bonded to the silicon centre.

Function	Shift range (normally)
$R_3Si\text{-}O$	+ 44 → -44 (+12)
$R_2Si(O\text{-})_2$	+ 14 → -74 (-20)
$RSi(O\text{-})_3$	-37 → -99 (-57)
$Si(O\text{-})_4$	-71 → -114

Table 6 Chemical shifts regions of Si-O containing compounds

In cyclic systems the degree of ring strain has a pronounced effect on the chemical shift. In general an enlargement of the ring leads to a reduction in ring strain and hence an upfield shift is observed in the case of electronegative bond partners of Si capable of π-bonding (*i.e.* O or N), but downfield in all others.

Compound	δ (ppm)	Compound	δ (ppm)	Compound	δ (ppm)
$[(CH_3)_2Si]_4$	-27.56	$[(CH_3)_2SiO]_3$	-9.90	$[Ph_2SiO]_3$	-33.80
$[(CH_3)_2Si]_5$	-42.13	$[(CH_3)_2SiO]_4$	-20.20	$[Ph_2SiO]_4$	-42.3
$[(CH_3)_2Si]_6$	-41.87	$[(CH_3)_2SiO]_5$	-22.80		
		$[(CH_3)_2SiO]_6$	-23.00		

Table 7 Effect of ring size on ^{29}Si NMR shifts

1.2.4 PROPERTIES OF THE SILANOL FUNCTION

A. ACIDITY

The greater acidity of silanols relative to carbinols was first demonstrated qualitatively in 1946 through the formation of sodium triethylsilanoate from triethylsilanol and sodium in xylene.[44] Fortunately modern spectroscopic techniques and acid/base titrations now afford a semi-quantifiable measure of their relative differences.

Silanol	Base	Free O-H stretch (cm^{-1})	Δυ (cm^{-1})
Me_3SiOH		3688	
	Me_3SiOH		189
	Et_2O		238
	C_6H_6		40
Et_3SiOH		3685	
	Et_3SiOH		185
	Et_2O		230
Ph_3SiOH		3677	
	Et_2O		319
	THF		333
$(HOMe_2Si)_2O$		3693	402
	$(HOMe_2Si)_2O$		
$(HOPh_2Si)_2O$		3681	284
	$(HOPh_2Si)_2O$		
$Me_2Si(OH)_2$		3693	
	dioxane		239
$Bu_2Si(OH)_2$		3680	
	Et_2O		263
$Ph_2Si(OH)_2$		3670	
	Et_2O		314

Table 8 IR data for common silanols and their complexes

An estimate of the proton donating ability (acidity) of the OH groups can be obtained by reacting the silanol (or carbinol) with a reference base. A comparison of the change in silanol (carbinol) O-H

stretching frequency in the "free" state (very dilute solutions, *ca.* 0.001 M in CCl_4) and upon H-bonding to the base indicates the relative acidities.

This method is based on the approximate relationship between the energy of the H-bond (ΔH) and the shift in frequency ($\Delta\upsilon$) of the hydroxyl bands which accompanies the formation of the bond: the stronger the bond, the greater the shift.[9, 45] Changes in frequency shift ($\Delta\upsilon$) recorded for compounds in a wide range of aldehydes, ketones and ethers imply that silanols are roughly twice as acidic as the corresponding carbinols.[46] For example, $\Delta\upsilon$ has been calculated as 226 cm^{-1} when Ph_3SiOH complexes with acetone yet the change in wavenumber is only 120 cm^{-1} for Ph_3COH.

The relative order of acidities can be defined as arylsilanols > alkylsilanols > arylcarbinols > alkylcarbinols with the acidity being further enhanced by the addition of electron withdrawing substituents to the silicon centre.[47]

Solvent effects in regard to the Si-OH bond have also been observed. A reduction in the solvent polarity results in a decrease in the free OH-solvent interaction, and thus the increased stretching frequency is accompanied by a decrease in the relative intensity of the band (table 9).

Silanol	Free OH in $CHCl_3$ (cm^{-1})	Free OH in CCl_4 (cm^{-1})	Free OH in C_6H_{12} (cm^{-1})
Ph_3SiOH	3667	3686	3691
Me_3SiOH	3675	3697	3706
Bu_3SiOH	3671	3695	3702

Table 9 Solvent effects on IR data for silanols

In cases where measurement of solution shifts are not possible due to the likely condensation of the species, relative acidities have been measured in the gas phase. H_3SiOH is reported to be more acidic than H_3COH.[47] In donor solvents, *eg.* DMSO, ^1H NMR chemical shifts δ (ppm) correspond well with the acidity of the silanol[48] whilst proton NMR spectra in non-coordinating solvents also reveal that the greater protonic character in Me_3SiOH *cf.* Me_3COH is due to the smaller amount of shielding of the OH proton. Although ^1H spectra provide a rough indication of the acidity of a compound it remains a less accurate indicator than pKa measurements, as chemical shifts are not solely dependent upon acidity.

B. Basicity

Comparison of the frequency shift of silanols in their "free" state and after reaction with a more powerful proton donor (normally phenol) reveals the relative order of basicities to be alkylcarbinols > alkylsilanols > arylcarbinols ≈ arylsilanols.

Thus whilst silanols are nearly twice as acidic as alcohols they remain almost as basic. For many years it was ***postulated*** that the enhanced acidity affects of silanols arose through the delocalisation of negative charge over the $[R_3SiO]^-$ moiety. This involved the donation of the *p*-electrons of the oxygen to the vacant *d*-orbitals of Si, whilst the basic properties emanated from the availability of the lone pair of electrons still present on oxygen. More recent studies[49] have questioned the validity of these arguments and these are covered in a later section (see section 1.2.5.F).

Silanol	Acid	Free O-H stretch (cm^{-1})	$\Delta\upsilon$ (cm^{-1})
Me_3SiOH	PhOH	3688	216
Et_3SiOH		3685	228
Ph_3SiOH		3677	175

Table 10 Selected IR data for silanol and their phenol complexes

Hence in view of their high acidity and relatively high basicity it is to be expected that under the right conditions and with suitable species, silanols will readily form H-bonded compounds.[47,50]

1.2.5 STRUCTURAL STUDIES

A. INTRODUCTION

A rich vein of structural studies are possible within the realms of silanol compounds due to their highly polarised nature and the wide variety of functionalities that may be appended to the silicon centre. Unfortunately cystallographic studies have been hindered by the difficulty in producing crystals of suitable quality for accurate determination of the position and orientation of the proton within the OH group. In the absence of such data structural discussions centre on the separations between O···O, O···N, O···F and O···π_{system}, and through interrogation of IR spectra. Intramolecular H-bonding gives rise to bands in the range of 3600-3610 cm^{-1} in dilute CCl_4 solutions, *e.g.* $HO(SiPh_2)_nOH$ for n = 4, 5, or 6 interactions between the aromatic system and the SiOH proton produces absorption bands at 3608, 3605 and 3605 cm^{-1} respectively. Systems exhibiting intermolecular SiOH···π interactions are distinguished by a change in free SiOH frequency from around 3580 cm^{-1} in the solid state to approximately 3650-3680 cm^{-1} in solution. Compounds that do not contain intramolecular H-bonding may manifest intermolecular SiOH···π system interactions in aromatic solvents. Thus an absorption for Ph_3SiOH in the solid state appears at 3200 cm^{-1} but shifts to 3685 cm^{-1} in CCl_4 and 3620 cm^{-1} in C_6H_6.

Most silanols exhibit a broad similarity in Si-O bond lengths, and Si-O-X (X = H, O, N, Cl, F *etc*) bond angles, with the main differences arising through differences in the type of H-bonded network.

The diverse nature of the networks is dictated by the number of Si-OH functionalities and the steric bulk of silicon substituent. Thus 3-D systems and layered aggregates are evident for silanols with small functionalities whilst self association into chains or discrete oligomers is favoured by silanediols with bulky substituents on silicon. In siloxanediols the structural differences again lie in patterns of solid-state H-bonding and hence the intermolecular associations. For compounds with small organic functionalities on silicon, double stranded chains predominate whilst large substituents on silicon engender the formation of sheets.

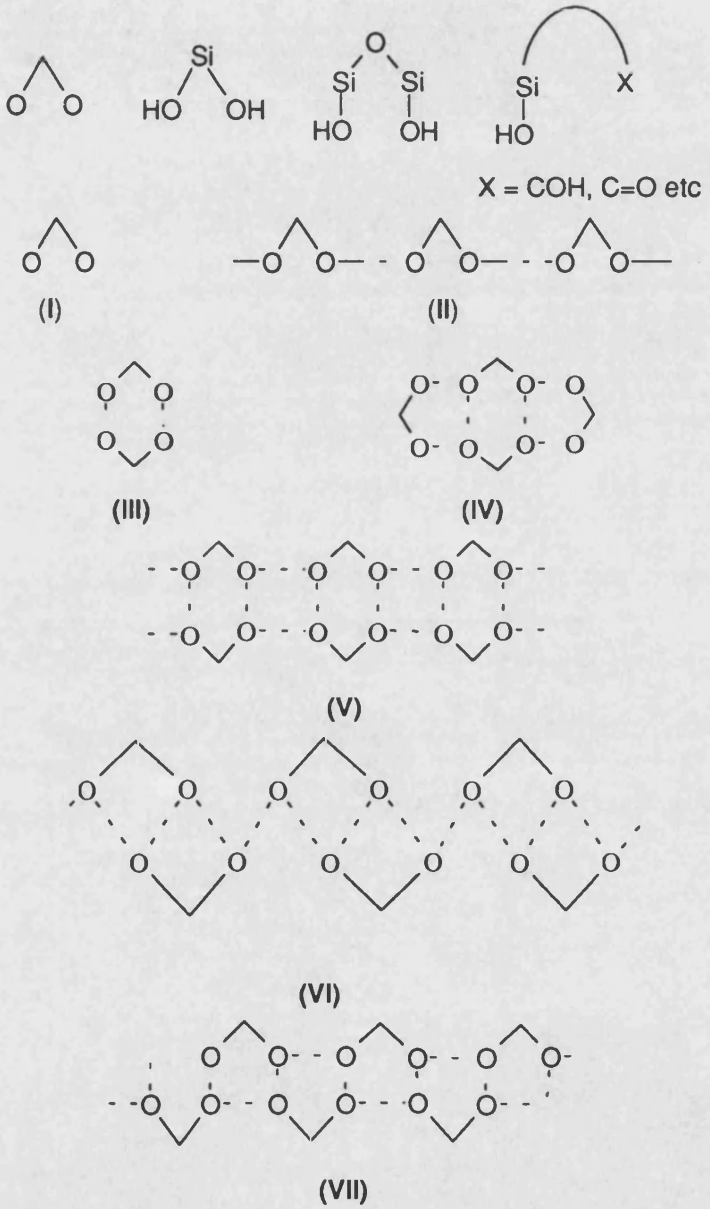


Figure 3 Common structural patterns occurring in silanol compounds

Thus in compounds containing more than one silanol function, or those that contain one SiOH group and have a second available H-bonding site, generally form only a small number of structural types based around the patterns shown above. Structures of type (I) are rarely observed as sterically de-

manding ligands are required to ensure that inter- or intramolecular associations do not occur. If the second available H-bonding site is a COH, C=O group or contains a nitrogen atom, then networks of type (II) are created. Systems with large substituents, *i.e.* ^{t}BuPhSi(OH)$_2$ or $(C_5Me_5)_2Si(OH)_2$ favour small discrete units (III-IV) whilst those containing less demanding functionalties allow chains (V-VII). In highly polar silanols, such as those containing triol functions double sheets or small clusters are often observed.

B. COMPOUNDS CONTAINING ONE SILANOL GROUP

Compounds containing only a single silanol group display a diversity of networks depending upon the bulk of the appended susbstituents as noted above.

In extremis highly hindered silanols such as (4) (figure 4) form no intermolecular bonds whilst in (5) there is some IR evidence for the formation of intramolecular bonds with the protons from the aromatic ring system.[51]

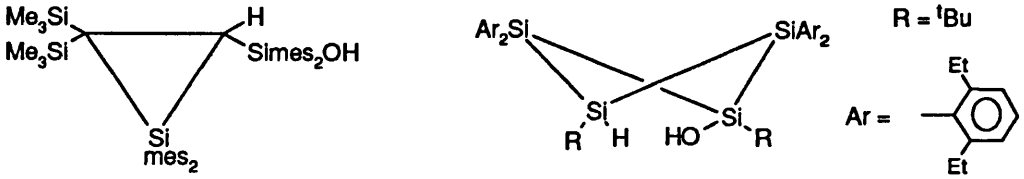


Figure 4 Hindered silanols containing no intermolecular bonds

A combination of tertiary butyl substituents with different groupings ensure that limited intermolecular associations exist. Thus a cyclic arrangement of discrete tetrameric units [O···O 2.756(9) Å, O···O···O 89.7°][52] is formed in ^{t}Bu$_2$Si(OH)F although investigation of the structure revealed that the fluorine does not participate in H-bonding. Monolithiated[53] and sodium[54] salts of ^{t}Bu$_2$Si(OH)$_2$ form solvated crystals of [^{t}Bu$_2$Si(OH)(OLi)·THF]$_4$, and [^{t}Bu$_2$Si(OH)(ONa)·THF]$_6$ in which the unit cell comprises cubic tetrameric and prismatic hexameric motifs respectively, with the free SiOH group bound to THF molecules.

Larger arrays are observed in less hindered silanols, hence triphenylsilanol, Ph_3SiOH, contains 16 molecules within the unit cell which consists of two independent flattened tetrahedral arrangements of Si atoms. The structure of the unit cell is shown in figure 5, with the O···O distances evaluated as ranging from 2.637(5) to 2.684(6) Å.[55]

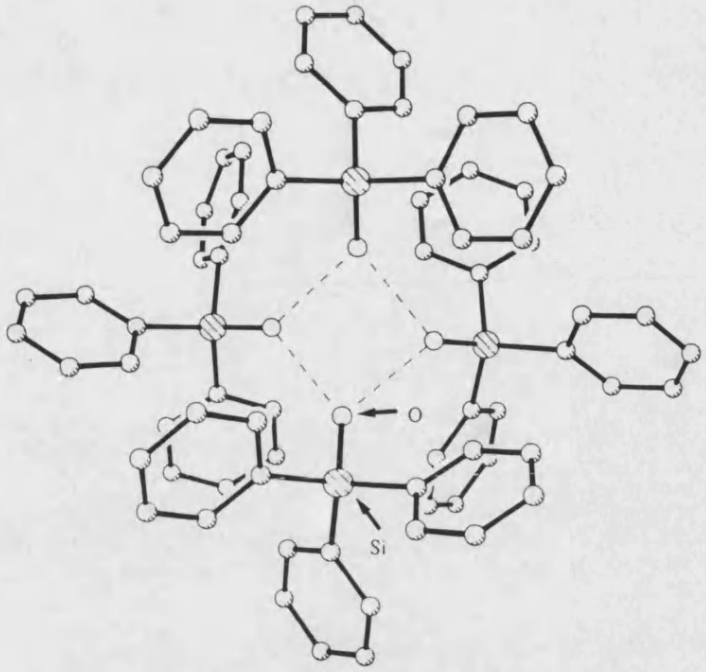


Figure 5 The unit cell of triphenylsilanol.

H-bonding arising from intermolecular associations between an external SiOH function and oxygen atoms in a cyclic ring system can lead to the formation of a chain structure.[56]

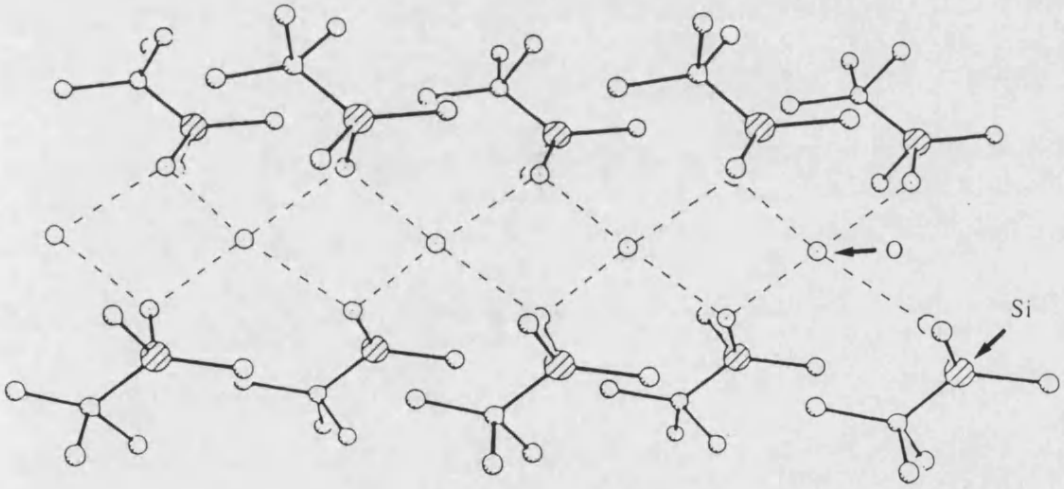


Figure 6 H-bonding arrangement in $[^tBuMe_2SiOH]_2{\cdot}H_2O$.

Chains are also formed on complexation of silanols by external agents. Hence a crystalline hemihydrate, $[^tBuMe_2SiOH]_2{\cdot}H_2O$ is formed upon the absorption of water by liquid $^tBuMe_2SiOH$. A structural determination, figure 6, reveals the formation of H-bonded chains with the water molecules acting as linkages between the chains.[10a, 57]

C. COMPOUNDS CONTAINING TWO SILANOL GROUPS

(i) Silanediols

Studies of silanediols have been impeded by their ability to undergo spontaneous self condensation reactions. However the structures so far reported are defined by very precise steric interactions, with only small differences in the bulk of substituents attached to silicon producing disparate structural motifs. Extended H-bonded arrays are not observed with very bulky substituents, for example [*cis*-bis(2,2′-bipyridine)$_2$Si(OH)$_2$], [(Tsi)SiPh(OH)$_2$] where Tsi = $(Me_3Si)_3C$, [$(\eta^1$-$C_5Me_5)_2Si(OH)_2$], and [(Tsi)SiF(OH)$_2$] give rise to a dihydrate[58], a dimer[59] and tetrameric[60] and hexameric units respectively. Similar but not identical ladder structures (type **V**) are formed by $R_2Si(OH)_2$ (where R = ^{i}Pr, ^{t}Bu, and *c*-C_6H_{11}).[4, 61] Pairing of the disilanol leads to the formation of dimers which then link through further intermolecular associations to build the chain structure. A notable exception is that of $^i Bu_2Si(OH)_2$ which exists as a discotic liquid,[29, 44] with crystallisations from various solvents failing to provide suitable crystals for a structure determination. However IR data is indicative of a type (**V**) array. The columnar structure[62] of $Ph_2Si(OH)_2$ is formed by the stacking of the hexameric unit cell which comprises two pairs of three independent molecules related by a centre of symmetry.

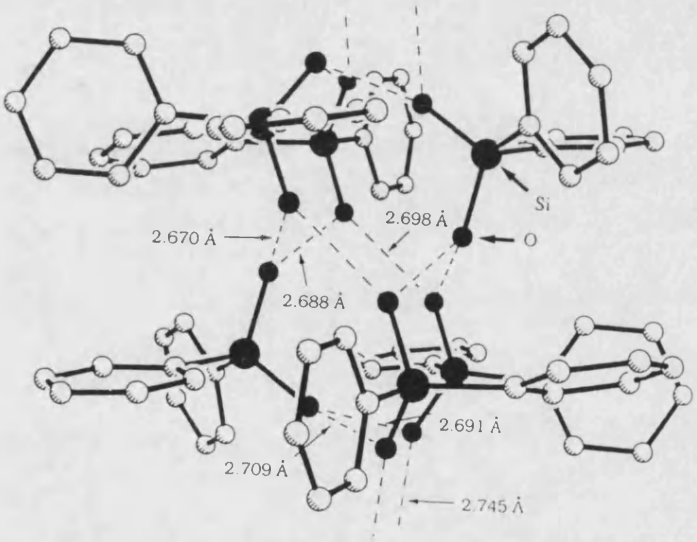


Figure 7 H-bonding leading to the columnar structure of $Ph_2Si(OH)_2$

H-bonding results in a chair shaped ring of oxygens (figure 7) containing alternating short (2.670 Å), medium (2.688 Å) and long (2.698 Å) O···O, distances with further H-bonding linking the hexamers above and below to form a column in which the OH point towards the centre and the Ph groups point outwards.

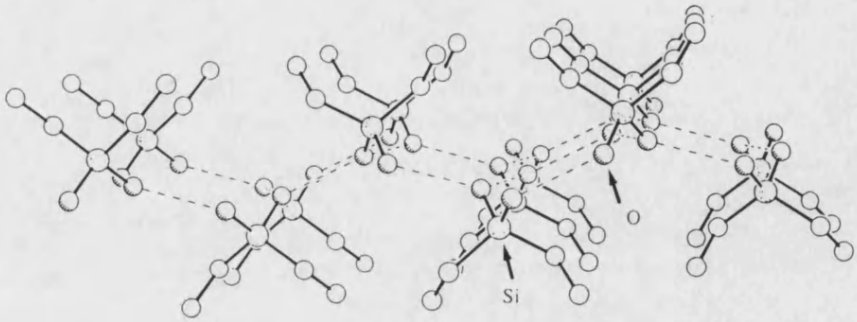


Figure 8 Sheet formation in $Et_2Si(OH)_2$

Extensive H-bonding leads to the formation of an infinite sheet arrangements which exist in compounds such as $Et_2Si(OH)_2$ which contain small ligands appended to the silicon centre.[63]

(ii) Siloxanediols

Structural studies of the disilanol $Cy_7Si_7O_9(OH)_2OSiMe_2Ph$ (where Cy = *c*-C_6H_{11}) (**5**), formed by the silylation of Fehers trisilanol compound (**1**) (figure 1), reveal a dimeric structure containing both intra- and intermolecular bonds (figure 9).

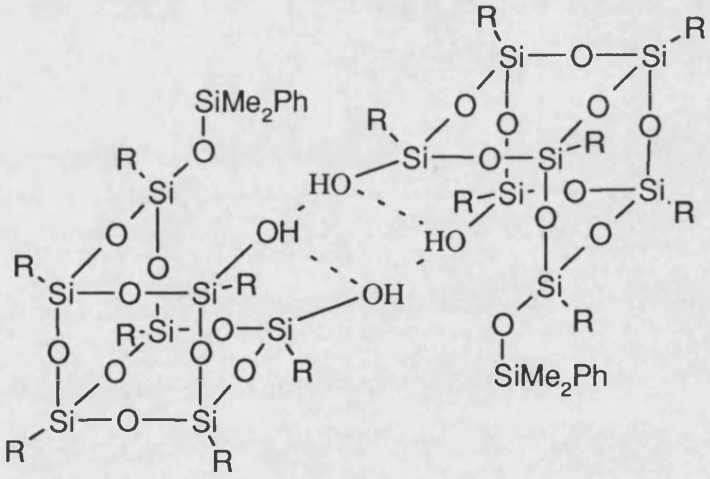


Figure 9 Dimeric nature of $[Cy_7Si_7O_9(OH)_2OSiMe_2Ph]$ (**5**)

The O···O distances of 2.722 Å and 2.670 Å for intra- and inter- molecular bonds respectively are comparable with those observed in $HO(SiPh_2O)_3H$.[21c, 64]

The bulk of the substituents again determines the degree of H-bonding within acylic silanol systems. Hence for dihydroxydilsiloxanes (where R = Me, Et, ^{n}Pr and Ph)[3, 65] arrangements of type (**VII**) are observed (figures 10 and 11). X-ray diffraction and IR studies of $HO(SiMe_2O)_2H$ indicate that no intramolecular H-bonding exists.

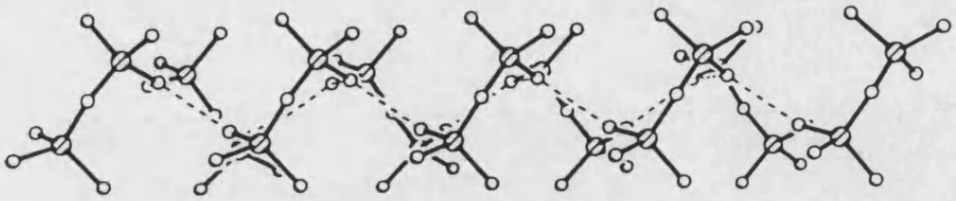


Figure 10 H-bonding arrays in the structure of $HO(SiMe_2O)_2H$

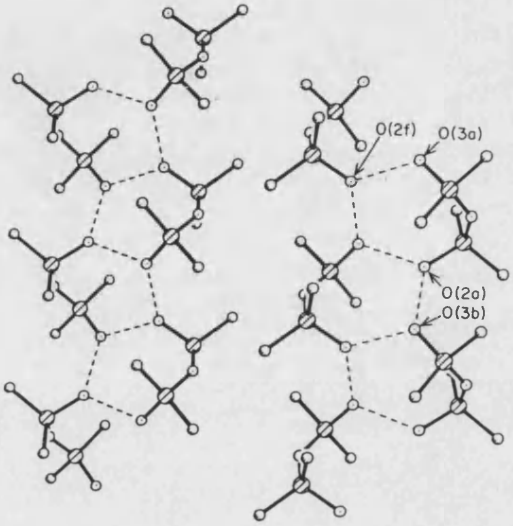


Figure 11 H-bonding arrays in the structure of $HO(SiMe_2O)_2H$

Larger functionalities, *i.e.* ^{i}Pr[66] and *c*-C_5H_9 cause silanols to adopt structures conforming to those of type (**VI**). Longer chain siloxanes, exemplified by $HO(SiPh_2O)_3H$, the structure of which was determined in this department,[67] contain both inter- and intra- molecular interactions and provides an interesting comparison with the structures of α,ω-dihydroxyoligosilanes, dihydroxydisiloxanes and silanediols.

D. COMPOUNDS CONTAINING THREE SILANOL GROUPS

Slow hydrolysis of $CySiCl_3$ (where Cy = *c*-C_6H_{11}) in an acetone/water mixture produces a partially hydrolysed cage trisilanol compound which is used as a model to represent specific silica planes. Structural studies by Feher reveal the silanol to exist as a H-bonded dimer with only intermolecular associations and O···O distances of 2.63-2.75 Å.[16b]

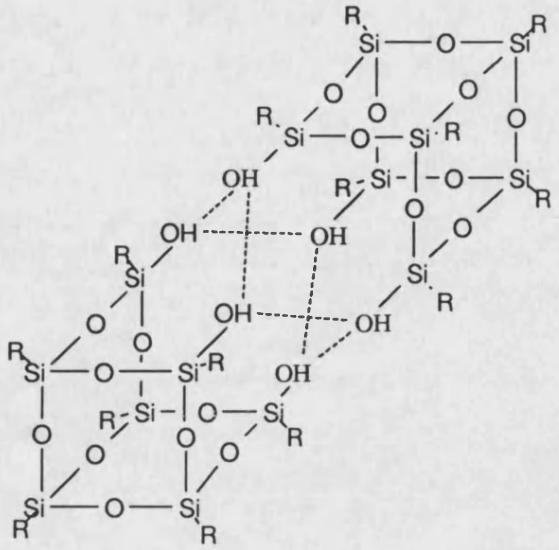


Figure 12 The dimeric nature of $[Cy_7Si_7O_9(OH)_3]$

In contrast the careful hydrolyses of $CpSiCl_3$ and $CySiCl_3$ produce $[CpSi(OH)_3{\cdot}0.5\ H_{22}O]$[68] and $CySi(OH)_3$ respectively. Both form layered structures with the latter exhibiting a sheet structure formed through a double layer of molecules joined in head to head fashion.[15] The structure is maintained by the hydrophobic outer surface preventing further interactions between the sheets. In $^tBuSi(OH)_3$ interaction between the sheets is prevented by alternating ^{t}Bu groups above and below the sheet in a manner similar to $[^tBuSi(OH)_2]_2O$ (figure 15).

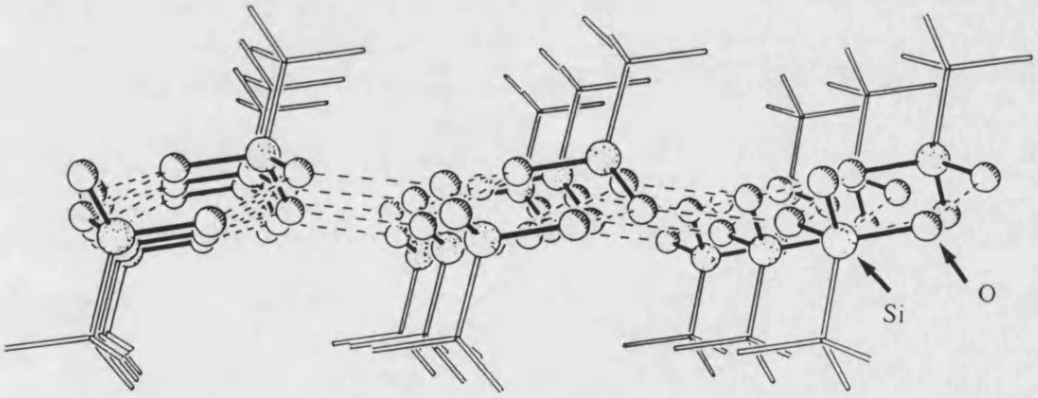


Figure 13 Sheet structure of $^tBuSi(OH)_3$

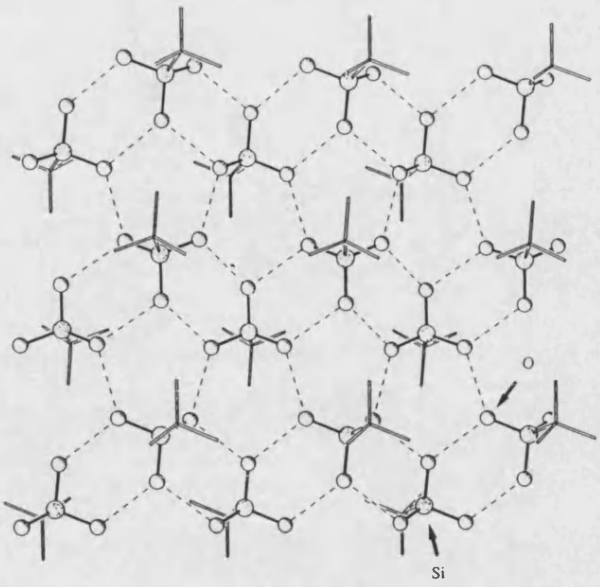


Figure 14 Sheet structure of $^{t}BuSi(OH)_3$

Even bulkier substituents $(PhMe_2Si)_3C$, $(Me_3Si)_3C$, and $(Me_3Si)_3Si$ provide extra stability to silanols leading both to greater difficulty in preparation and so to discrete tetra- and hexameric structural motifs.[3, 69]

E. COMPOUNDS CONTAINING FOUR SILANOL GROUPS

Due to their highly unstable nature only three such compounds have been isolated. Of particular interest is $[^{t}BuSi(OH)_2]_2O$ which is formed when $^{t}BuSiCl_3$ is hydrolysed in a strongly alkaline solution and contains an Si-O-Si bond angle of approximately 180°.[50]

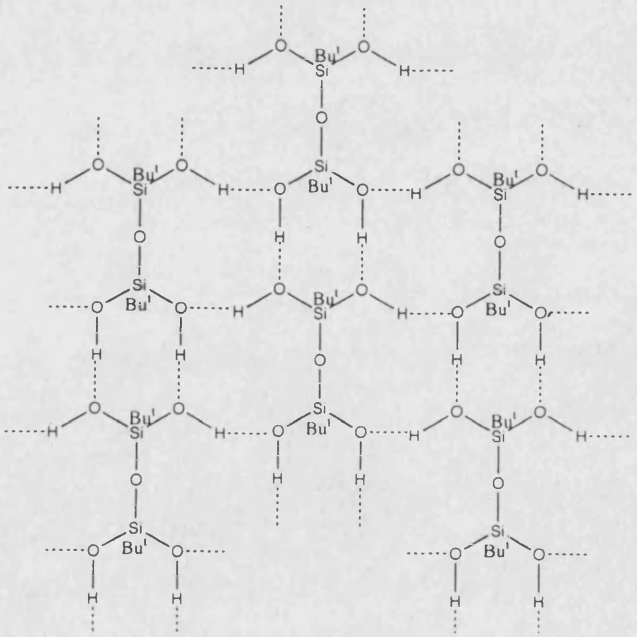


Figure 15 Sheet structure of $[^{t}BuSi(OH)_2]_2O$

Intermolecular H-bonding create hydrophobic regions between the sheets formed by the chains of molecules in which ^{t}Bu groups alternate above and below the layer (figure 15).[50]

X-ray data for the norbonylsiloxane (figure 16) is of insufficient quality to accurately determine hydrogen positions. However indications are that the arrangement is consistent with the formation of a H-bonded dimeric species,[70] but IR studies have indicated the possible presence of both inter- and intra- molecular bonds,[71] and so further structural studies are required.

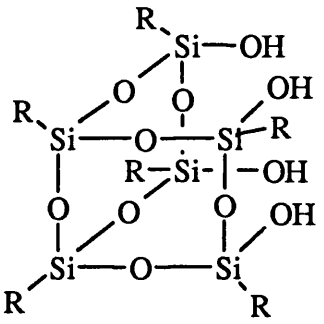


Figure 16 Cage structure of norbornylsiloxane

In the final example considered, that of the tetrasilanol, $[(HOSiMe_2)_4C]$, an extended 3-D network is adopted. It contains four independent molecules in the unit cell, each of which exhibit two intramolecular bonds, and these are arranged in alternating layers which link to form sheets. Further intermolecular bonds connect the sheets to form the 3-D network.[72]

F. THEORETICAL CONSIDERATIONS

In the case of the highly unstable and non-isolable simple silanols, $H_nSi(OH)_{4-n}$ (n = 0-3) calculations provide an invaluable insight into bonding data. The majority of bond lengths are calculated to be shorter (1.64 ± 0.03 Å) than the 1.76 Å expected from the sum of the covalent radii. For a long time the strengthening and shortening of bonds between silicon and an electronegative element was assumed to involve the donation of electron density (*via* the lone pair of electrons residing on the electronegative atom) into the vacant *d*-orbitals residing on silicon. This relatively simple panacea for delocalisation of charge was invoked in attempts to explain

- The planar geometry of the weak lewis base trisilylamine, $N(SiH_3)_3$, *cf.* the pyramidal geometry of $N(CH_3)_3$
- The wide bond angle at oxygen in silyl ethers (140-180º), and their basicity in comparison to alkyl ethers
- The higher acidity and relatively high basicity of silanols in comparison with carbinols

More recent studies reduce emphasis on the role of the empty silicon *d*-orbitals and instead attribute the strength and length of the bond to its high polarity.[73] Later *ab initio* calculations refine these

theories further and yield good agreement with experimental data.[49] In the case of the silyl ethers the phenomena previously attributed to O($p\pi$)→Si($d\pi$) donation is reported to be caused by mixing of the frontier orbitals of the silyl (or alkyl) groups with the electron lone pairs present on oxygen.

1.3 HETERO- SILOXIDES AND SILOXANES

1.3.1 INTRODUCTION

Catalytically active transition metal centres supported by silica substrates are utilised within a diverse array of modern technological hetero- and homogeneous processes. As a result commercial importance of such catalysts has stimulated an intense research interest in the surface modified entities formed at the interface of the catalyst.

All categories of silica substrate are known to bind discrete molecular species to the bulk surface through reactions with an array of surface silanol (Si-OH) functions present at the substrate interface. The nature of the interface site is determined by a number of factors, *i.e.* the number and acidity of the silanol functions available and these can define the catalytic activity and selectivity of the tethered species. Unfortunately despite the recent advances in physiochemical and spectroscopic techniques, bulk metal-silica interactions at the atomic level remain difficult to define. *Ergo* identification of key 're'active process intermediates leading to the elucidation of detailed reaction mechanisms currently remain at best vague.

A wider perception of the reaction chemistry occurring at the interface can be undertaken through the preparation and characterisation of model systems containing transition-metal macromolecules. Here effective tailoring of the model support with a desired metal centre reveals detailed information pertaining to the electronic and steric effects of the substrate on the catalysts activity. Thus monodentate siloxides are used to replicate the effect of tethering a metal entity to a single surface site, bidentate silanols and siloxanes for geminal and vicinal couplings whilst cage compounds such as Fehers trisilanol mimic binding sites containing three or more hydroxyl functions. The impact of such interactions upon the electronic unsaturation of the metal centre can be ascertained by considering the strength of the O($p\pi$)→M($d\pi$) effects using bond length data.

1.3.2 PREPARATION OF HETEROSILOXIDES

There are four major routes utilised in the production of hetero- siloxides and siloxanes, of which the first two are most commonly and successfully used. The synthetic methods pertaining to the isolation of metallasilsesquioxanes are discussed in the next section.

A. METAL-HALIDE SALT ELIMINATION

This route is the most commonly utilised entry into early transition metal hetero- siloxide and siloxane compounds. Generally addition of the alkali metal silanolates (M = Li, Na, K) generated *in situ*, or pre-prepared, to the metal chloride is carried out at low temperature. Etheral solvents are used to solubilise the metal chloride precursors. As a result high yields (65-90%) of products are normal.

Reaction of anionic bifunctional silandiolates, *e.g.* $Ph_2Si(OM)_2$ and $[Ph_2Si(OM)]_2O$, where M = Li, Na can lead to chain expansion of the silanolate and formation of a spirocyclic transition metal. The outcome is determined by the nature of the metal chloride and the alkali metal appended to the silanolate but the mechansims leading to chain expansion are not well understood.[74]

Compound	Reactants	Ref
$[M(OSi^tBu_3)_nCl_{5-n}]$ M = Ti, Ta, Sc, Nb (6)	MCl_5, $NaOSi^tBu_3$,	75
$[ZrCl_2(OSiPh_3)_2(DME)]$ (7)	$ZrCl_4$, $NaOSiPh_3$	76
$[Hf\{OSi(C_6H_4Me\text{-}2)_3\}\cdot Li(Et_2O)_2$ (8)	$HfCl_5$, $Li[OSi(C_6H_4Me\text{-}2)_3]$	77
$[Nb\{OSi(C_6H_4Me\text{-}2)_3\}\cdot 1.5\ Et_2O$ (9)	$NbCl_5$, $Li[OSi(C_6H_4Me\text{-}2)_3]$	77
$[Cr(silox)_3]$ (10)	$CrCl_3$, Li(silox)	8
$[CrO_2(OSiPh_3)_2]$ (11)	CrO_2Cl_2, 2 $NaOSiPh_3$	78
$[Rh(COD)_2(Ph_3SiO)_2]$ (12)	$RhCl_2(COD)_2$, $NaOSiPh_3$	79
$[Ta[OSi(C_6H_4Me\text{-}2)_3]Cl_4]\cdot 1.5\ Et_2O$ (13)	$TaCl_5$, $Li[OSi(C_6H_4Me\text{-}2)_3]$	80
$[TaCl_4(silox)]$ (14) **$[TaCl_2(silox)_3]$ (15)**	$TaCl_5$, Li(silox) $TaCl_5$, 2-5 Li(silox)	81
$[Mn(silox)_2]\cdot LiCl$ (16)	$MnCl_2$, Li(silox)	8
$[Cu\{OSi(O^tBu)_3\}_2(py)_2]$ (17)	$CuBr_2$, 2 $NaOSi(O^tBu)_3$, py	82

Table 11 The synthesis of heterosiloxides *via* salt elimination

Compound	Reactants	Ref
$[(py)_2Li]_2$-μ-$[Mg\{Ph_2SiO\}_2O][\{Ph_2SiO\}_3O]$ (18)	$MgCl_2{\cdot}THF_2$, $[Ph_2Si(OLi)]_2O$, py	83
$[SnCl_2\{O(SiPh_2O)_2\}_2$-μ-$\{Li(THF)_2\}_2]$ (19)	$SnCl_4$, 1-3 $[Ph_2Si(OLi)]_2O$, THF	84
$[Sn\{O(^tBu_2SiO)_2\}_2]$ (20)	$SnBr_4$, $[^tBu_2Si(OLi)]_2O$, THF	54
$[THF_2Sn\{O(SiPh_2O)_3\}_2]$ (21)	$SnCl_4$, 1-3 $[Ph_2Si(ONa)]_2O$, THF	54
$[Ti\{O(SiPh_2O)_3\}_2(py)_2]{\cdot}2\ C_7H_8$ (22)	$TiCl_4$, 2-3 $[Ph_2Si(OLi)]_2O$	85
$[Ti\{O(SiPh_2O)_2\}_3\{Na(py)\}_2]{\cdot}py$ (23)	$TiCl_4$, 3 $[Ph_2Si(ONa)]_2O$, py	74
$Li[M\{O(SiPh_2O)_2\}_2]{\cdot}3py{\cdot}1.5\ C_7H_8$ M = Zr, Hf (24)	$ZrCl_4$, 2 $[Ph_2Si(OLi)]_2O$	74
$[Hf\{O(Ph_2SiO)_3\}_2(py)_2]{\cdot}2\ C_6H_5Me$ (25)	$HfCl_4$, $[Ph_2Si(ONa)]_2O$, THF	74
$[VO\{O(SiPh_2O)_2\}$-μ-$\{Li(THF)_2\}_2]$ (26)	VCl_4, 3 $[Ph_2Si(OLi)]_2O{\cdot}2$ THF	86
$[Cr\{O(SiPh_2O\}_2$-μ-$Na(THF)_2\}_2]$ (27)	$CrCl_2$, $[Ph_2Si(ONa)]_2O$, THF	87
$[Mo(O)_2(\mu\text{-}OSi^tBu_2O)]_2$ (28)	MoO_2Br_2, $^tBu_2Si(OLi)_2$	88
$[py_2Li]$-μ-$[Co\{O(OSiPh_2)_2\}_2]$ (29)	$CoCl_2$, $[Ph_2Si(OLi)]_2O$, py	89
$[TMEDALi]_2$-μ-$[Co\{O(OSiPh_2)_2\}_2]$ (30)	$CoCl_2$, $[Ph_2Si(OLi)]_2O$, TMEDA	89

Table 12 Silanediolate reactions leading to spirocyclosiloxanes

Compound	Reactants	Ref
$[Ti(OSiPh_3)_4]$ (31)	$Ti(OC_4H_9)_4$, Ph_3SiOH $TiCl_4$, Ph_3SiOH, NH_3	90 91
$[Ti\{(^tBuO)_3SiO\}_n(O^iPr)_{4-n}]$ (32)	$Ti(O^iPr)_4$, n $(^tBu_3O)_3SiOH$	92
$[M(OSiPh_3)_4]\cdot DME$ M = Ti, Zr, Nb, Ta, Ce (33)	$M(O^iPr)$, Ph_3SiOH	93
$[ZrCp_2(OSiPh_3)_2]$ (34)	Cp_2ZrMe_2, 2 Ph_3SiOH	94
$[Zr(OSiPh_3)_4]$ (35)	$Zr[CH_2Si(CH_3)_3]_4$, 2 or 4 Ph_3SiOH	94
$[V(O)(OSiPh_3)_n(CH_2SiMe_3)_{(3-n)}]$ (36)	$V(O)(CH_2SiMe_3)_3$, n = 1 -3 Ph_3SiOH	95
$[Co(OSiPh_3)(\mu\text{-}OSiPh_3)(THF)]_2$ (37)	$[Co\{N(SiMe_3)_2\}_2]_2$, 4 Ph_3SiOH	96
$[Tl(\mu\text{-}OSiPh_3)_4]$ (38)	Tl(OEt), $Ph_3Si(OH)$	111
$[M(\mu\text{-}OSiPh_3)(OSiPh_3)_2]_2$ M = Y, La, Ce (39)	$M[N(SiMe_3)_2]_3$, Ph_3SiOH	98
$[\{Y(OSiMe_2{}^tBu)_2(HOSiMe_2{}^tBu)\{Y(OSiMe_2{}^tBu)\}(\mu\text{-}OSiMe_2{}^tBu)_2]$ (40)	$[Y\{N(SiMe_3)_2\}_3]$, 3.5 $HOSiMe_2{}^tBu$	97
$[Y(OSi^tBuAr_2)\{N(SiMe_3)_2\}_2]$ (41)	$Y[N(SiMe_3)_2]_3$, $HOSi^tBuAr_2$	98
$[K(18\text{-}c\text{-}6)][Y(OSiPh_3)_4]$ (42)	$[Y(OSiPh_3)_3]_n$, $[K(18\text{-}c\text{-}6)(OSiPh_3)]$	
$[K(\eta^2\text{-}DME)(\eta^1\text{-}DME)][Y(OSiPh_3)_4(\eta^2\text{-}DME)$ (43)	$[Y(OSiPh_3)_3]_n$, $[K(thf)_{0.2}(OSiPh_3)]$	
$[M(OSiPh_3)_3(THF)_3]$ M = Y, La, Ce, Pr, Nd, Y (44)	$M[N(Me_3Si)_2]_3$, Ph_3SiOH	99
$[M(MeSiO)_n(O^iPr)_{3-n}]$ M = Gd, Er (45)	$M(OC_3H_7)_3$, $CH_3SiOOCH_3$	100
$[U(\eta^5\text{-}C_5H_5)(OSiPh_3)_3]$ (46)	$[U(\eta^5\text{-}C_5H_5)_3(NEt_2)]$, Ph_3SiOH	101

Table 13 Metathesis reactions leading to heterosiloxides

B. METATHESIS REACTIONS

Metathesis reactions are commonly used for electropositive early transition metal that form extremely strong SiO-M bonds (tables 13 and 14).

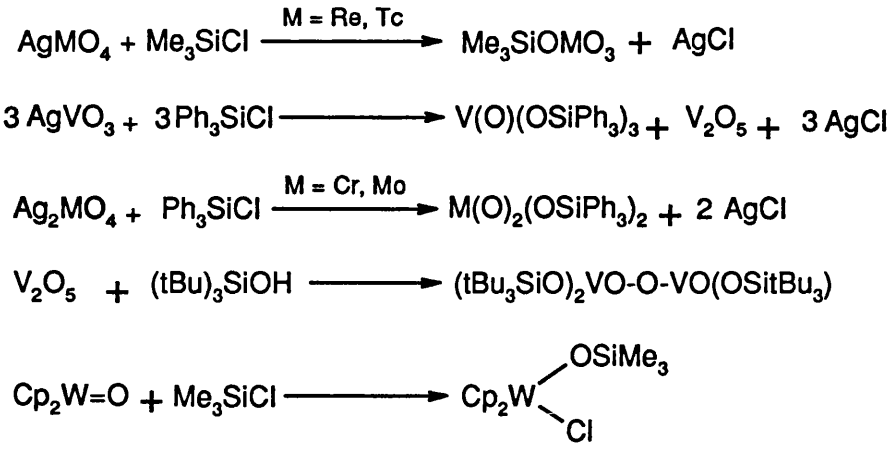
Compound	Reactants	Ref
$[Ti\{O(SiPh_2O)_2\}_2]$ (47) decomposes to $[Ti\{O(SiPh_2O)_3\}_2(py)_2]\cdot 2\ C_7H_8$ (48)	$TiCl_4$, 2 $[Ph_2Si(OH)]_2O$, py	85
$[NEt_2H_2]_2[M\{O(SiPh_2O)_2\}_3]$ (49-50) M = Zr, Hf	$M(NEt_2)_4$, 6 $Ph_2Si(OH)_2$,	85
$[Ti\{O(SiPh_2O)_4\}_2]$ (51)	$Ti(O^iPr)_4$, 8 $Ph_2Si(OH)_2$ $Ti(OBu)_4$, $Ph_2Si(OH)_2$	90, 102
$[MCp_2(\mu\text{-}OSiPh_2O)]_2$ M = Zr, Hf (52)	Cp_2MMe_2, $Ph_2Si(OH)_2$,	103
$[Ti(\mu\text{-}OSi^tBu_2O)(Me_2CHO)]_2$ (53)	2 $(^tBuO)_2Si(OH)_2$, 2 $Ti(OCHMe_2)_4$	104
$[Ti(C_5R_5)Cl_2OSi^tBu_2(OH)]$ R = Me_4Et, Me (54)	$[Ti(C_5R_5)Cl_3]$, $^tBu_2Si(OH)_2$, NEt_3	105
$[(C_5H_4Me)ClTiOSi^tBu_2O)\}]$ (55)	$2[Ti(C_5H_4Me)Cl_3]$, 2 $^tBu_2Si(OH)_2$, NEt_3	105
$[MOSi^tBu(OR')(C_5R_5)_2X]$ M = Ti, Zr, Hf, R = H_4Me, R' = H, X = Cl, F(56)	$[M(C_5R_5)_2X_2]$, $^tBu_2Si(OR')_2$	105
$[V(O)Cl(\mu\text{-}OSi^tBu_2O)_3]$ (57)	$VOCl_3$, $^tBu_2Si(OH)_2$	88

Table 14 Bidentate metathesis reactions for generating heterosiloxanes

The reactions find great utility in the production of aluminosiloxanes and lanthanide siloxide and siloxanes as the less polar nature of both precursors greatly aids their solubility in non-donor media. As a result it is not difficult to remove co-ordinated solvents, which is very important in applications where volatility and purity of material are at a premium, *i.e.* CVD and sol-gel deposition techniques.

C. DIRECT SILYLATION OF M=O FUNCTIONS

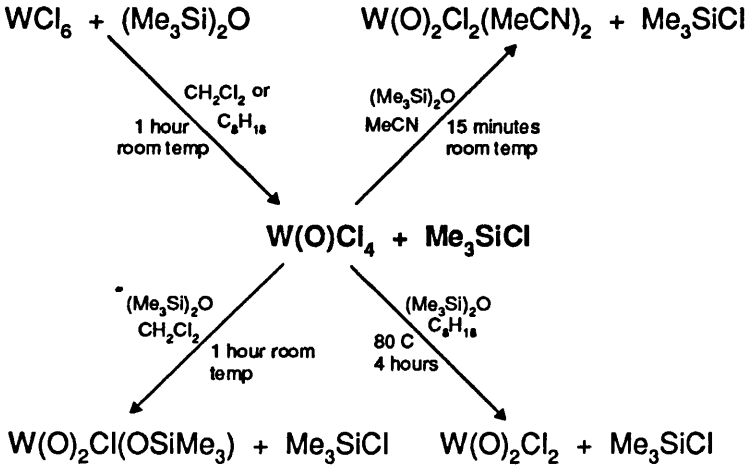
Trimethyl- and triphenyl- chlorosilanes are reported to react directly with M=O functions to produce metal-siloxy species in good yields. This is exemplified in scheme 2.[106] The lattice energies of the silver metalates and the very high M=O bond strength are important in determing the outcome of the reactions. Thus whilst silver chromate reacts smoothly at room temperature, molybdenum requires heating, whereas silver tungstate does not react. The lower reactivity of the tungstate is reflected in its higher M=O bond strength and thus lower lattice energy.



Scheme 2 Silyation of metal oxo species

D. CLEAVAGE OF AN Si-O FUNCTION

Early high oxidation state transition metal and lanthanide complexes are reported to undergo reactions with silylethers and cyclic siloxanes. Thus cleavage of hexamethyldisiloxane by high oxidation state, chromium,[107] molybdenum and tungsten halides not only provides a convenient route to high purity (oxo)halide moities but also results in the formation of a tungsten siloxide moiety (scheme 3).[108]



Scheme 3 Reactions of silylethers and tungsten (oxo)halides

The existence of ring opening reactions leading to the formation of heterosiloxanes was serendiptiously discovered from the reaction of $AlMe_3$ with silicone grease, but this observation has been widely developed to produce an excellent route for the production of aluminosiloxane species.[109]

Ytterbium,[110] thallium[111] and samarium[112] complexes are reported to react with THF containing silicone grease as an impurity. Further investigations of the last reaction have highlighted the propensity of the smaller, strained rather than the larger, less strained cyclic components of silicone grease to undergo ring opening reactions.

$$[Yb(C_3N_2NHMe)_2(C_5H_4Me)] + [Me_2SiO]n \xrightarrow{THF,\ 25\ ^oC}$$

$$[\{Yb(\eta^2\text{-}C_3N_2HMe_2\text{-}3,5)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}OSiMe_2C_3N_2HMe_2\text{-}3,5)(\eta\text{-}C_5H_4Me)\}_2] \textbf{ (58)}$$

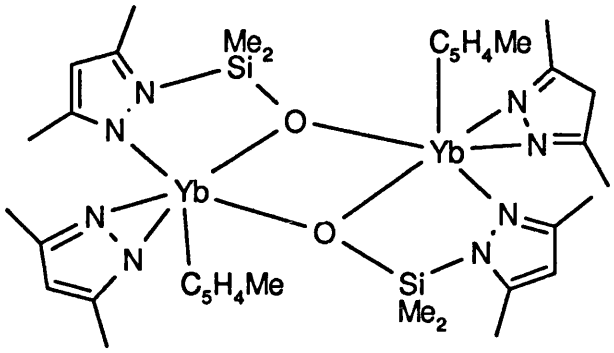


Figure 17 The novel ytterbium siloxide (**58**)

E. Co-condensation reactions

Some early transition metal species (M = Cr, Mo) are also known to undergo co-condensation reactions with silanols and alkoxy-, aryloxy- or amino- alkylsilanes, *i.e.* [113]

$$CrO_3 + 2\ Ph_3SiOH \rightarrow CrO_2(OSiPh_3)_2 \qquad \textbf{1.10}$$

1.3.3 STRUCTURAL STUDIES

A. Introduction

Structural studies are usually undertaken in siloxide chemistry in order to elucidate electronic aspects of bonding *via* consideration of the Si-O-M bond angle and the length of the Si-O and M-O linkages. These topics are discussed later through their effect on catalytic activity in monodenate early transition metal and metallasilsesquioxane complexes. This section concentrates primarily on the bonding modes and structural motifs adopted by main group, transition metal and lanthanide siloxide complexes.

Simple silanoate compounds, those containing a single Si-O function, form monodenate, μ, μ_3-bonding modes depending upon the bulk of the attached organic ligands and the nature of the appended metal. Bidentate disilanols ligands containing only a single Si atom, usually act as bridge between two metal centres although they may undergo chain expansion and act in a similar manner to longer chain silanolate (n = 2, 3, 4) precursors in forming spirocyclic complexes.

B. Main group siloxides and siloxanes

Structural studies of alkali metal siloxides have been developed recently to complement those of transition and lanthanide siloxides in which they serve as efficient $[R_3SiO]^-$, $[O(SiR_2)_nO]^{2-}$, [n = 1, 2,

3, 4, R = Me, Et, ^{t}Bu, Ph, $PhMe_2$] transfer agents. Synthesis of group I metal siloxides is readily achieved by direct combination with the metal (M = Na, K), metal hydride (M = Na, K), metal alkyl (M = Li) or strong base (M = Na). Less reactive group II metals (Ba, Mg, Ca) require the presence of ammonia to act as a solubilising agent.

Whilst group I metal siloxides are primarily generated *in situ* during the synthesis of transition metal and lanthanide siloxides, many have recently been isolated and structurally characterised in an attempt to explain their reactivity. $MOSiR_3$ (M = Li, Na, K, R = Me, Et, Ph) species are often isolated as amorphous powders from non-coordinating solvents, but readily form crystalline solids in the presence of a co-ordinating solvent or crown ether.[114] Larger metal cations tend to form bigger aggregates, *cf.* $[Li(\mu\text{-}OSiPh_3)(\eta^2\text{-}DME)]_2$ (**59**) with $[K_4(\mu_3\text{-}OSiPh_3)_3(\mu\text{-}OSiPh_2(\eta^1\text{-}Ph)(\eta^2\text{-}DME)]_2(\mu\text{-}DME)$ (**60**). Bridging siloxide modes are common because the nucleophilicity of the oxygen is retained due to minimal electronic effects of the $M^+\text{-}O^-$ bond. Group II alkaline metal siloxides include, $[Ba_3(OSiPh_3)_4(THF)_6]\cdot 0.5$ THF (**61**), $[KBa_2(OSiPh_3)_5]\cdot(DME)$ (**62**) and $[Ca_2(OSiPh_3)_4(NH_4)]\cdot 0.5\ C_7H_8$ (**63**) all of which adopt a triangular, $XM(\mu\text{-}X)_3M$ structure.[115] A noticable feature of their chemistry is the preference for uncharged molecular species to near exclusion of charge seperated salts.

Bidentate ligands containing two Si-O functionalities have inspired a great deal of recent research due to their ability to undergo ring expansion and form spirocyclic compounds in the presence of metal halide moieties. $[Ph_2Si(OLi\cdot py)]_2O$ (**64**), $[\{Ph_2Si(OLi)\}_2O\cdot 3(C_4H_8O)]_\infty$ (**65**) are readily synthesised by the addition of ^{t}BuLi solutions of $[Ph_2Si(OH)]_2O$. Structural studies reveal that both compounds (**64**) and (**65**) are based on a dimeric arrangement involving a 12-membered $Li_2Si_4O_6$ ring consisting of three 4-membered lithio-oxane rings in a folded ladder arrangement.[116]

C. TRANSITION METAL SILOXIDES AND SILOXANES

Most transition metal triorganosiloxide contain simple monodentate siloxide ligands (see tables 11 and 13). However the presence of small organic functionalities on silicon, engenders the formation of dimeric species for aluminium (R = Me, Et), rhodium (R = Me, Ph)[79, 117] and molybdenum (R = Me) complexes.[118]

Bidentate, disilanol compounds tend to form bridging structures with early transition metal centres, *i.e.* the eight and twelve membered rings in the metallasiloxanes (**66**) and (**67**) (figure 18).

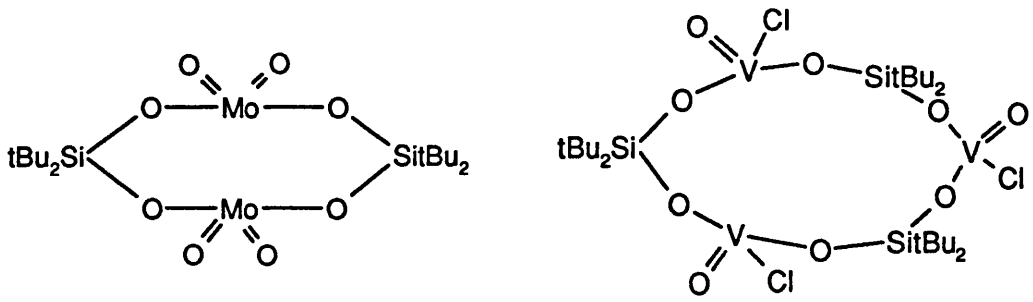
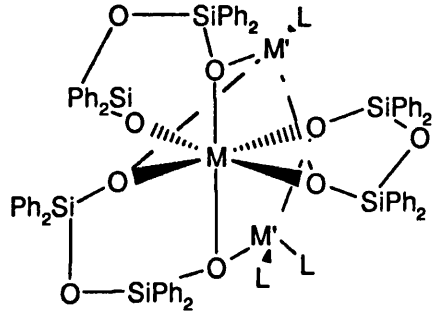
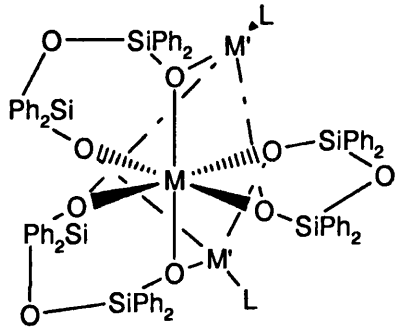


Figure 18 Bridging bidentate siloxides

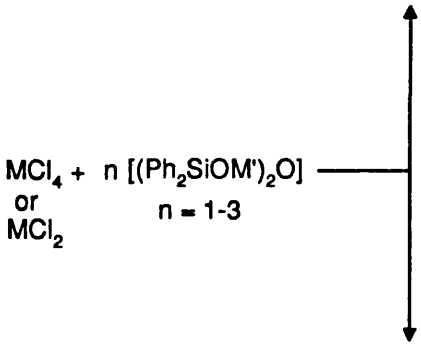
There are a rapidly growing number of metallasiloxanes incorporating the tetraorganodisiloxanediolate ligand $[(Ph_2SiO)_2O]^{2-}$.[83-87, 89, 102a, 119]



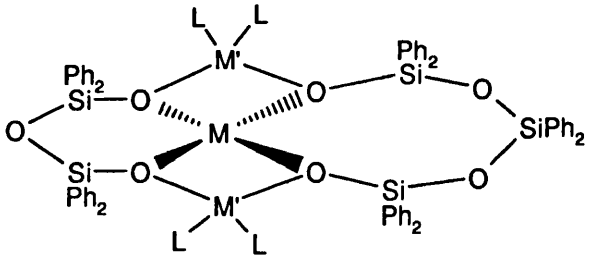
M = Zr, M' = Li, L =py
M = Hf, M' = Li, L = py



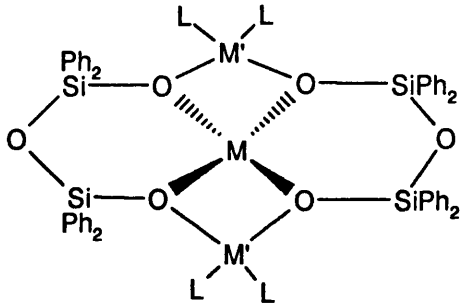
M = Ti, M' = Na, L =py



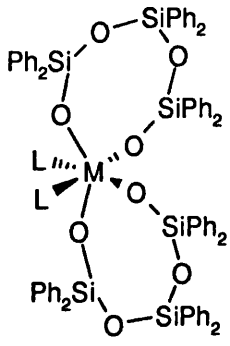
MCl_4 + n $[(Ph_2SiOM')_2O]$ — n = 1-3
or
MCl_2



M = Mg, M' = Li, L = py



M = $SnCl_2$, M' = Li, L = THF
M = VO, M' = Li, L = THF
M = Cr, M' = Na, L = THF
M = Co, M' = Li, L = py, THF
M = Cu, M' = Li, L = py



M = Hf, M' = Na, L = py
M = Ti, M' = Li, L =py
M = Sn, M' = Na, L = THF

Figure 19 Spirocyclic early transition metallasiloxanes

Co-ordination of this ligand to a metal centre occurs *via* chelation, bridging or chelate-bridging modes. Of particular interest in this class of compounds are those containing the chelate and chelate-bridging modes formed during ring-expansion of $[(Ph_2SiO)_2O]^{2-}$ to yield the trisiloxanediolate ligand $[(Ph_2SiO)_3O]^{2-}$ (figure 19). In addition the mixed metal spirocyclic metallsiloxane, $[(py_2Li)$-μ-$\{(Co(OSiPh_2OSiPh_2O)_2 \cdot 2py\}$-$\mu$-$MnClpy]$ (**68**) has been isolated and structurally characterised.[120]

D. LANTHANIDE SILOXIDES

Structural studies of lanthanide siloxides have been hindered by the soft plastic like behaviour of the solids and the tendancy for disorder to occur in the attached pendant alkyl chains. ^{29}Si NMR is often utilised to identify terminal and bridging bonding modes despite the often poor solubility because of the limited structural data on these compounds.

Aggregate formation is witnessed in lanthanide siloxides containing even relatively bulky substituents, *e.g.* $[M(OSiR_2'R)_3]_n$ (M = Y, La, Ce, R = R' = Ph and R = Me, R' = ^{t}Bu).[97, 121] These compounds are dimers containing two terminal and one bridging siloxide per metal atom,[98a,b] however in the presence of donor ligands octahedral *fac*-$[M(OSiPh_3)_3(L)_3]$ (M = Ce, Pr, Nd, Y, L = thf, py) (**69**), $[Y(OSiPh_3)_3(OPBu_3)_2]$ (**70**) complexes are formed. Bulkier ligands containing pendant amine functionalities have been used to synthesise monomeric siloxide moieties for use in the production of relatively volatile, non-aggregate precursors for sol-gel and CVD deposition techniques. These include $[Ln\{OSi(^tBu)_{3-n}[(CH_2)_3NMe_2]_2\}_3]$ (**71**) where Ln = Y, n = 1 or 2 and Ln = Ce, n = 1 which exhibit trigonal bipyramidal geometry around the metal centre. The siloxide ligands occupy the equatorial sites with the pendant amine functionalities occupying the axial sites.[98c, 122]

1.3.4 PROPERTIES AND APPLICATIONS OF HETEROSILOXIDES

A. EARLY TRANSITION METAL METATHESIS CATALYSTS

(i) Introduction

Low valent, low co-ordinate early transition metal complexes are widely employed as catalysts in classical olefin and acetylene metathesis systems,[123] due mainly to their high reactivity and the fact that with few exceptions a metal centre binds a substrate whilst transforming it. Hence historically the preparation of electronically unsaturated complexes, *i.e.* those with electron counts less than 16/18e$^-$ has commanded much attention.

Previous attempts to generate reactive, low coordinate metal centres concentrated on complexes containing bulky neutral ligands, such as PR_3 (*e.g.* R = ^{i}Pr, Cy, ^{t}Bu) and π-hydrocarbons, both neu-

tral (*e.g.* η^6-C_6R_6) and anionic (*e.g.* η^5-C_5Me_5, η^8-C_8H_8). However these ancillary ligands tend to electronically and sterically saturate a metal centre, rendering it "soft". This is especially true of the ubiquitous cyclopentadienyl ligand which has been observed in every niche of organometallic chemistry over many years. Replacement of cyclopentadienyl, a $5e^-$ donor, by a sterically similar, lesser donating alkoxide or siloxide ligand enables the preparation of complexes possessing inherent electronic unsaturation. These transition metal compounds supported exclusively by hard π-donor ligands often possess fundamentally different and potentially more useful properties and reactivity patterns than their low valent congeners.

The work featured in this section has been reported principally by two groups, those of Chisholm and Wolczanski, and illustrates the synthesis, influence and reactivity of low valence early transition metal complexes supported by the bulky, hard, anionic "tritox" $[^tBu_3CO]^-$ and "silox" $[^tBu_3SiO]^-$ ligands.

(ii) Steric Aspects of Alkoxides and Siloxides

Initial investigations by Tolman estimated the cone angle of cyclopentadienyl to be 136°, but more recent revisions have approximated it to be closer to 130°.[75] In order to maintain steric control of reactivity, the alkoxide or siloxide analogue is required to mimic the steric constraints imposed the cyclopentadienyl ligand.

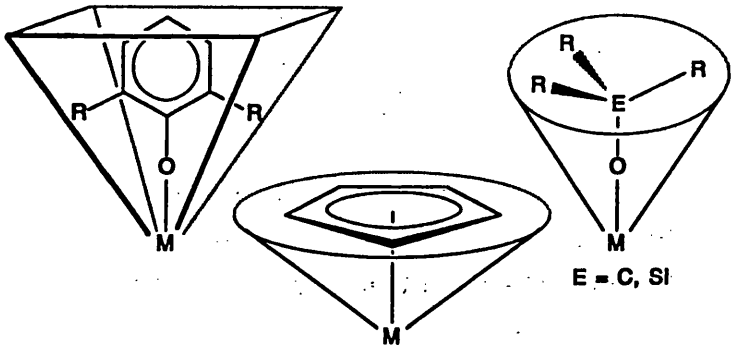


Figure 20 Spatial perception of the cyclopentadienyl ligand and its alternatives

Thus interest has focused on ligands which combine groups substantially greater in size than for example ^{t}Bu (the simple alkoxide $[^tBuO]^-$ has a cone angle of less than 90°) but which also reproduce and fill a true conical region of space just as in symmetric cyclopentadienyl derivatives. Initially the wedge shaped bulky 2,6-disubstituted aryloxides were investigated but attention has now shifted towards siloxides and alkoxides possessing three equivalent bulky R groups triangulated about the O-C(Si) vector (figure 20).

(iii) Alkoxide and Siloxide Electronic Features

In principle alkoxide and cyclopentadienyl ligands are electronically analogous. Linear combinations of C π-orbitals comprise σ- and π-donor orbitals of cyclopentadienyl, (figure 21), whilst alkoxides and siloxides bind principally through a σ-type orbitals, such as the *sp* hybrid indicated, and *via* π-donation of two *p*π-orbitals that are perpendicular to the M-O vector.

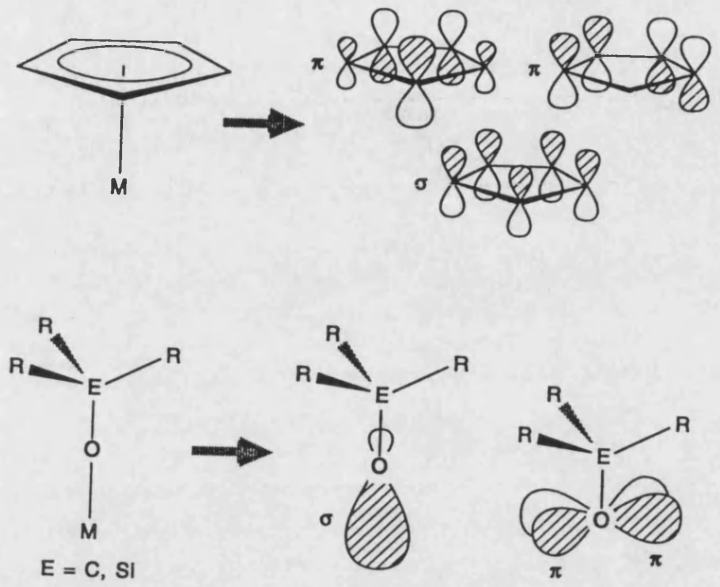


Figure 21 Donor orbital analogy of Cp to an alkoxide or siloxide ligand

By converting this molecular orbital depiction to a simple EAN counting scheme the implication is that alkoxides and siloxides are $5e^-$ donors, akin to cyclopentadienyl.

In investigating this hypothesis structural information has been used to support claims of metal-ligand multiple bonding. Particular emphasis is placed on both the M-O-E (E = C, Si) angle and M-O bond length, with an approximately linear M-O-E bond or shorter M-O bond, believed to imply the involvement of both *p*π-orbitals in O(*p*π)→M(*d*π) donation. However a more circumspect approach is required, as Rothwells' identification of the lack of correlation between M-O-E angle and d(M-O) suggests that inferences drawn solely on these criteria may be incorrect.

A better understanding results from Extended Hückel Molecular Orbital (EHMO calculations) which compare the energies of the metal σ- and π-acceptor orbitals with those of the donor ligand. Thus for early metals, O(*p*π)→M(*d*π) interactions are stronger in the second and third rows, where the overlap of appropriate orbitals is better than in the first row. This is counteracted to a lesser extent by a better energy match between the orbitals of the less electropositive first row metals and oxygen. On moving from left to right across the periodic table, orbital overlap declines but the interacting orbitals approach one another energetically.

In practice, experimental observations are more indicative of alkoxides and siloxides acting as $3e^-$ donors, especially when conducting formal electron counts. Our understanding of alkoxide and siloxide donation is dominated by two factors. First σ-bonding for M-OR (M = early transition metal) ligation is extremely strong, primarily due to the large ionic component of this formally covalent bond. Secondly the strength of both σ- and π- interactions is dependent upon the electrophilicity of the metal centre. Hence in the case of extremely low coordination, electron deficient centres, the strength of both types of interaction are increased to accommodate the demands of the metal. In this respect, just like any versatile ligand in organometallic chemistry, the typical alkoxide/siloxide can adapt to its environment.

A comparison of the two ligands reveals on balance a silyl rather than an alkyl substituent on the oxygen renders the R_3EO (E = C, Si) ligand less donating as a consequence of the more electropositive influence of silicon. The charge delocalising effects of the Si-O bond are also thought to attenuate the $O(p\pi)\rightarrow M(d\pi)$ donation usually ascribed to the ROM unit. Thus, relative to alkoxides, less basic siloxides bind to a metal with a slightly more ionic character. Hence the general electronic consequences of utilising a siloxide rather than alkoxide ligand are manifested in a greater electrophilicity at the metal centre. The limited spectroscopic data available indicates that siloxide ligands electronically influence a metal centre in roughly the same manner as aryloxides[124] with both being substantially better at supporting reduced metal centres. The combination of potent reduction potential with retention of electrophilicity is responsible for the unusual reactivity patterns evident in low valent silox derivatives. XPS data indicates that the silox ligand renders a metal centre approximately 0.5 eV more electrophilic than either a chloride or cyclopentadienyl ligand.[124] Such observations lead to a simplified description of siloxides, as a pseudohalide with large but adjustable steric parameters.

(iii) Tritox and Silox Ligands

Tritox is easily produced in a single step procedure, with distillation of the crude mixture followed by recrystallisation from MeOH yielding pure material.

$$^tBuC(O)OMe + 2\ ^tBuLi \xrightarrow[(ii)\ H^+,\ H_2O]{(i)\ -78\ ^oC,\ hexane} {}^tBu_3COH + {}^tBu_2CHOH \qquad \textbf{1.11}$$

Deprotonation to the lithium salt suitable for metathesis reactions occurs readily upon reaction with ^nBuLi.[75]

A study of the degree of substitution occurring in early transition metal halide complexes indicates that when attached to a metal centre, tritox occupies a symmetric, approximately 125° cone of space.

Thus, metathesis of $TiCl_4$ under stoichiometric control yield both *mono-* and *bis-* tritox derivatives but for the larger zirconium metal centre, *bis*-tritox moieties are formed independently of stoichiometry, and alcoholysis is required to yield the monosubsituted moiety (scheme 4).

$$ZrCl_4 + 2Li(tritox) \xrightarrow[8hr,\ -LiCl\ 80\%]{Et_2O,\ 25\,^oC} ZrCl_3(tritox)_2.Li(OEt_2) \xrightarrow[-LiCl]{\text{hexane rextal}} ZrCl_2(tritox)_2$$

Scheme 4 The metathesis of $ZrCl_4$ with Li(tritox)

Whilst titanium and zirconium alkoxides appear to display metastable behaviour, attempts to prepare niobium and tantalum analogues fail due to heterolytic cleavage of the C-O bond on tritox by the labile halide ligands present on the metals.

In comparison, silox, prepared by direct combination of silanol and sodium metal, reaction 1.12, shows noticable differences in metathesis reactions.

$$2\ {}^tBu_3SiOH + 2\ Na \xrightarrow[10hrs,\ 65\,^oC\ 80\text{-}90\ \%]{\text{hexanes}} 2\ {}^tBu_3SiONa + H_2 \qquad \textbf{1.11}$$

Stoichiometric control over the metathesis reactions of $TiCl_4$ with Li(silox), yields both mono- and disubstituted siloxides similar to tritox but the isolation of $[MCl_3(silox)_2]$ and $[MCl_2(silox)_3]$ (M = Nb, Ta) is also readily accomplished from reaction with MCl_5 (M = Nb, Ta).[125] Metathesis of zirconium tetrachloride is apparently independent of stoichiometric control and in this case readily forms the *tris*-silox product (reaction 1.13).[124]

$$ZrCl_4 + 3\ Na(silox) \xrightarrow[12hrs]{THF,\ 25\,^oC} ZrCl(silox)_3 + 3\ NaCl \qquad \textbf{1.13}$$

The implications therefore are that the cone angle of silox is greater than 120° but less than that of tritox, a feature attributable to the longer Si-O bond length placing the bulky ${}^tBu_3Si$ group further from the metal centre. However silox moieties exhibit higher thermal and chemical stability due to the stronger Si-O bond (~546 kJ mol^{-1}) in comparison to that of C-O (~378 kJ mol^{-1}). This renders the heterolytic scisson of the Si-O less likely than C-O, whilst nucleophilic attacks at the silicon centre are reduced by the bulk and electron donating properties of the t-butyl groups.

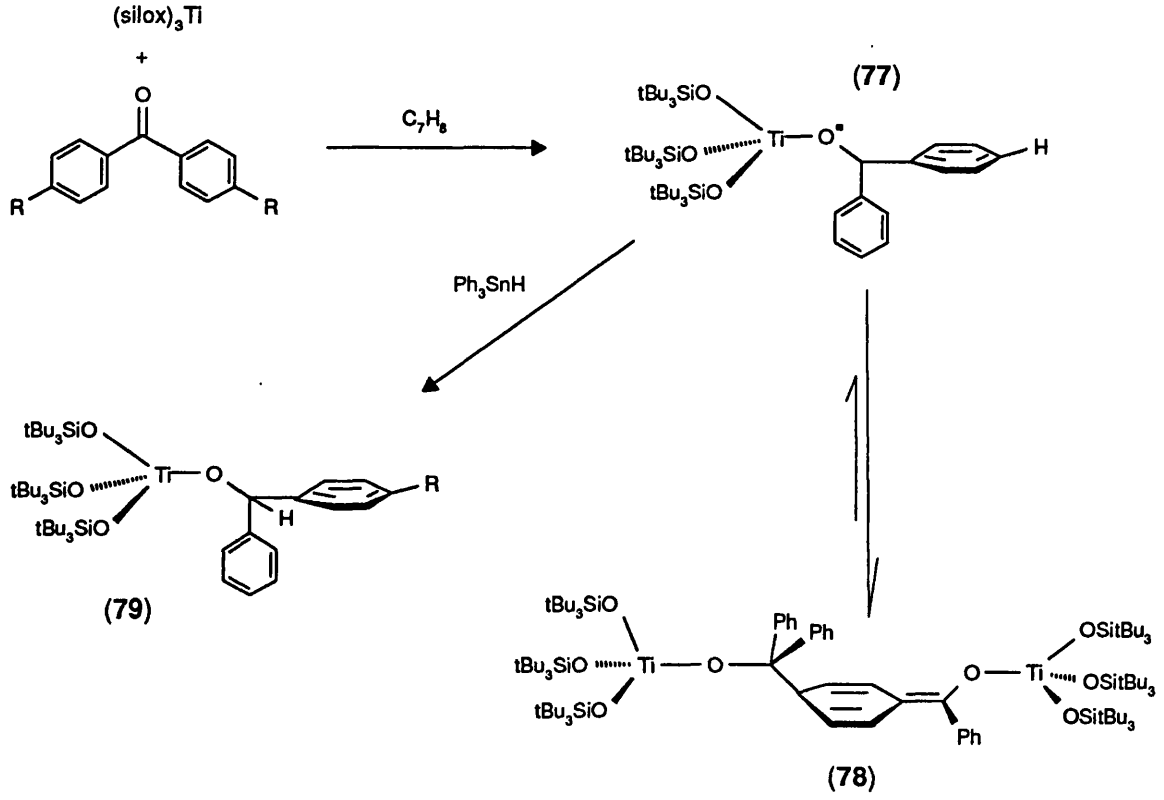
(iv) Low Valent Complexes

Reactive early transition metal siloxide complexes are generally prepared in good yields (70-80%) by the Na/Hg amalgam reduction of the appropriate silox-chloride compound (table 15).[75]

Compound	Precursor	Conditions
[Ti(silox)$_3$] (72)	TiCl(silox)$_3$	Na/Hg in DME. Recrystallise from C_7H_8.
[Ta(silox)$_3$] (73)	TaCl$_2$(silox)$_3$	Na/Hg in THF
[W=N^{t}Bu(silox)$_2$] (74)	W=N^{t}Bu$_2$(^{t}BuNH)$_2$	(i) HOSi^{t}Bu$_3$, C_6H_6, 3 days, 90 °C (ii) 2 HCl, C_6H_6, 3.5 days, 110 °C (iii) Mg reduction, Et_2O
[TaH$_2$(silox)$_2$]$_2$ (75)	TaCl$_3$(silox)$_2$	Na/Hg, H_2, C_7H_8, 15 days
[WCl(silox)$_3$]$_2$ (76)	NaW$_2$Cl$_7$(THF)$_5$	(i) Na(silox), THF, 100°C, 12 hours

Table 15 The synthesis of reactive transition metal silox derivatives

These highly reactive transition metal species form a wide range of adducts, *i.e.* [Ti(silox)$_3$] (**72**) is of particular interest in the investigation of intermediate ketyl species in transition metal mediated pinacol reactions (scheme 5).[126]



Scheme 5 Ketyl adducts of [Ti(silox)$_3$]

The reaction involves the transposition of an electron from titanium to the carbonyl carbon of the pinacol to yield (**77**), which in solution exists as a dimer (**78**) exhibiting a C-C bond between a carbonyl carbon and the para position of the phenyl. The reaction of the intermediate (**77**) with Ph_3SnH affords the diphenylmethoxide derivative, [TiOCHPh$_2$(silox)$_3$] (**79**) *via* H atom transfer.

[Ta(silox)$_3$] (**73**) provides a very rare example of a 3-coordinate, low valent, third row metal complex which normally exist as high valent, high coordinate species. This compound highlights the

proclivity for silox ligands to stabilise reduced metal centres, and it provides access to an intriguing range of adducts. Compound (**73**) reacts slowly in concentrated benzene solution to form [{Ta(silox)$_3$}$_2$(μ-C$_6$H$_6$)] (**80**) in low yield (7%) and with pyridine to form [Ta(silox)$_3$(η^2-(N,C)-py)] (**81**).[127] The latter is especially interesting as titanium, scandium and vanadium silox analogues all form η^1-pyridine complexes. EHMO calculations used to rationalise the unusual η^2-geometry indicate that large electron replusions between the N lone pair on pyridine and the filled d_z^2 orbital on Ta(silox)$_3$ force the pyridine bind as an olefin. The resulting strong Ta-C and Ta-N σ-bonds to what is formally considered a Ta^V centre offset the considerable disruption to the pyridine resonance energy. However, perhaps by far the most powerful indication of the reductive potential of (**73**) is the cleavage of CO in the carbonylation of [Ta(silox)$_3$] to give the dicarbide [{Ta(silox)$_3$}$_2$(μ-C$_2$)] (**82**), oxo [Ta=O(silox)$_3$] (**83**) and the ketylidene [TaCCO(silox)$_3$] (**84**).[128] Within certain limitations this reaction functions as a potentially good model of the first step, that of dissociative adsorption of CO, in the Fischer-Tropsch process. Oxidative addition reactions for [Ta(silox)$_3$] (**73**) with a large number of organic substrates are well documented and of particular interest are the reactions with pnictides, EPh$_2$ (E = N, P, As). The reactions proceed *via* an unstable pnictide hydride which spontaneously undergoes a 1,2-H$_2$-elimination to form Ta=EPh derivatives.[75]

Compound (**74**) [W=NtBu(silox)$_2$] is a planar, d^2 complex with a bonding arrangement similar to [Ta(silox)$_3$], consisting of a full compliment of π-bonding by available siloxide and imido donors with the exception of one non-bonding ligand *p*-orbital combination. The compound readily undergoes oxidative addition reactions with small olefin and acetylene organic substrates to yield η^2-complexes which bind strongly to the W^{IV} centre.[75]

(v) Metal-Metal Bonded Complexes

[TaH$_2$(silox)$_2$]$_2$ (**75**)[129] contains an unsupported Ta-Ta single bond, 2.720(4) Å, connecting two interlocked trigonal bipyramids which possess axial hydrides and basal silox ligands. It readily undergoes reaction with HCl and oxygen to form the bridging compounds [{TaCl(silox)$_2$}$_2$(μ-H)$_2$] (**85**) and [{TaH(silox)$_2$}$_2$(μ-O)$_2$] (**86**) respectively. [TaH$_2$(silox)$_2$]$_2$ also serves as a model for the Fischer-Tropsch process. Thus (**75**) severs the C-O bond of carbon monoxide during carbonylation to give a μ-CH$_2$ species, [{TaH(silox)$_2$}$_2$(μ-O)(μ-CH$_2$)] (**87**) which addition of a further equivalent of CO reforms to give a μ-formyl/μ-formaldehyde complex, [{TaH(silox)$_2$}(μ-CHO)(μ-CH$_2$O){Ta(silox)$_2$}] (**88**). After further work up, small oxygenated hydrocarbon products typical of the Fischer-Tropsch process are isolated. CO dissociation also occurs across the double bond of [(silox)$_3$W=W(silox)$_3$] (**76**) which cleaves the C-O bond to yield an oxo-μ-carbide [(silox)$_2$(O)W=C=W(silox)$_2$] (**89**).[130] The two W^{III} centres appear to model the first step of

the F-T process and are in good agreement with the work of Chisolm concerning the cleavage of CO by $W{=}W^{6+}$ complexes.[131] The ditungsten compound $[W_2(OSiMe_2{}^tBu)_6]$ (**90**) exhibits catalytic activity, as reaction with ethylene to a form polyacteylene constrasts well with the less reactive alkoxide $[W_2(OBu^t)_6]$ (**91**) which only forms $[W_2(OBu^t)_6(\mu\text{-}C_4H_4)]$ (**92**) on exposure to ethylene.[132] Reactions of (**90**) with a variety of organic substrates result in alkylidene bridged ditungsten complexes, *i.e.* $[W_2(\mu\text{-}C_2H_2)(OSiMe_2{}^tBu)_6]$ (**93**)[133] which may be further reacted with unsaturated hydrocarbon substrates.[134]

B. THE EFFECTIVENESS OF EARLY TRANSITION METAL SILOXIDE CATALYST MODELS

(i) Introduction

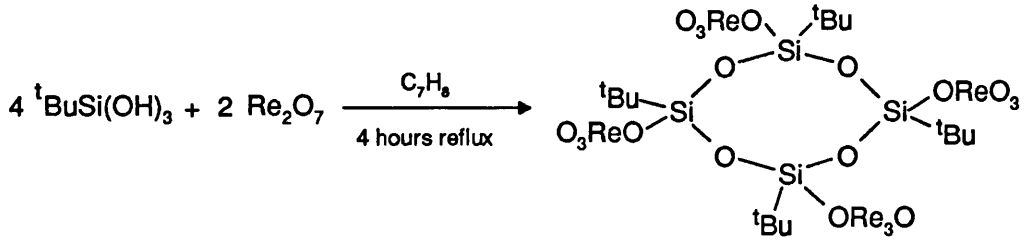
Studies in the fields of alkoxide and siloxide chemistry led by Wolczanski and Chisholm (*vide supra*) have highlighted the fact that the nature of the ligands present within the co-ordination sphere of a metal have a profound influence on its reactivity. The recent synthetic and mechanistic work demonstrates how alteration of the steric bulk of an alkoxide or siloxide ligand can lead to dramatic effects on the overall reactivity of the metal complex (see section 1.3.4.A). Therefore in order to obtain a realistic appraisal of the active species involved in catalysis the metal centre must be supported by a ligand or ligands capable of accurately replicating a silica interface.

Contemporary approaches to the modelling of metal-silica catalyst systems utilise metallasilsesquioxanes. These may be produced by co-condensation reactions or *via* coupling to an incompletely condensed polyhedral oligosilsesquioxane (POSS).[135] The latter approach utilises the ability of POSS ligands to support both main group and transition metal elements in a wide variety of co-ordination environments. Oligiosilsesquioxane compounds derive their ability to closely mimic silica surfaces from their ability to oligomerise in a manner related to that of highly siliceous material whilst retaining their reactive Si-OH functionalities. Thus upon coupling a metal centre to a POSS ligand the resultant polyhedral oligometallasilsesquioxane (POMSS) species possesses an extensive Si-O framework and hence similar electronic properties to a metal attached to a silica or siliceous substrate.[136] Their incompletely condensed structure also provides a more rigid and less mobile framework than the conventional monodentate siloxide ligands, so enabling the ligand to mimic the inflexible nature of silica surfaces in dictating the co-ordination geometry around the metal centre.[137]

(ii) Preparation of metallasilsesquioxanes

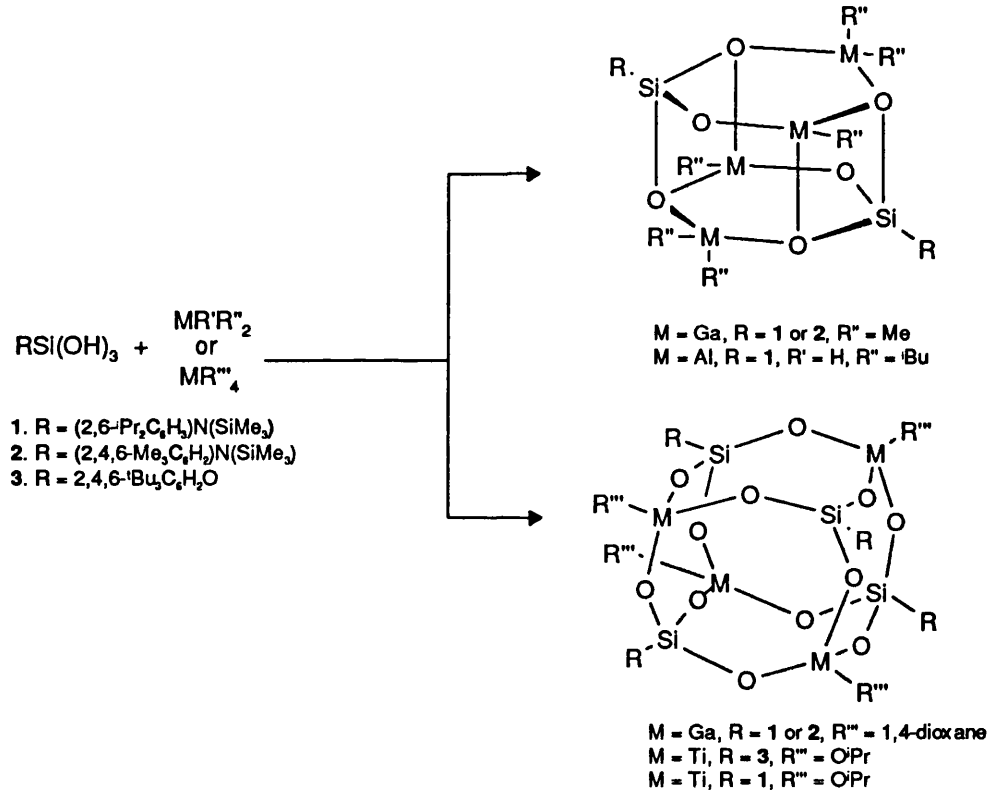
There are currently two general synthetic methodologies available to produce metallasilsesquioxane model complexes. The first is highlighted in recent attempts by Roesky *et al.* which involve the hydrolytic co-condensation of alkyl and aryl silanetriols with metal complexes. Work has led to the

isolation of eight-membered heterosiloxane rings systems incorporating aluminium or rhenium centres, *e.g.* scheme 6.[138]



Scheme 6 Hydrolytic co-condensation to produce cycloheterosiloxanes

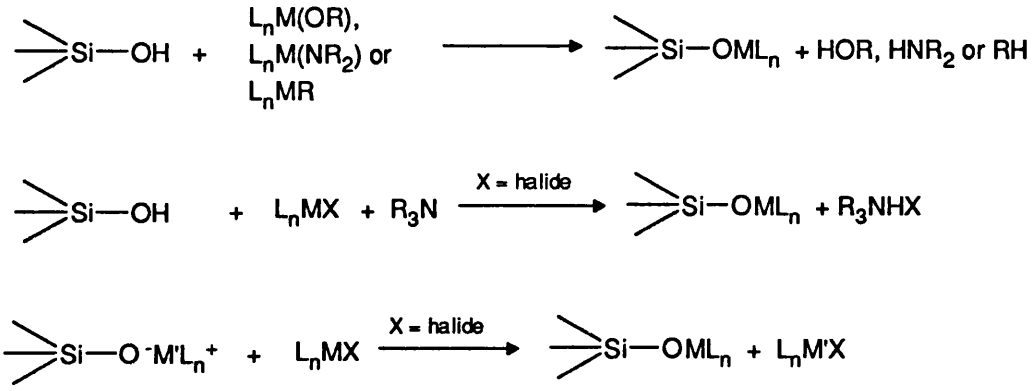
With more sterically demanding trisilanol precursors, co-condensation reactions with gallium,[139] titanium[140] and indium[141] complexes produce cage compounds in which the structure is defined by the reactant stoichiometries (scheme 7).



Scheme 7 Synthesis of metallasilsesquioxane cage compounds

This approach has the advantage of producing a ligand environment that electronically mimics siliceous materials but the profound influence the metal often has in directing the condensation process ensures that there is no guarantee of the product resembling anything close to a silica surface. A more assured approach in reproducing a silica interface relies on coupling POSS compounds, such as Fehers trisilanol (**1**), with a metal complex. This method not only ensures electronic conformity but the pre-made cage structure replicates the ability of silica surfaces to dictate the co-ordination geometry around the metal complex. The synthesis of POSS compounds by hydrolytic condensation

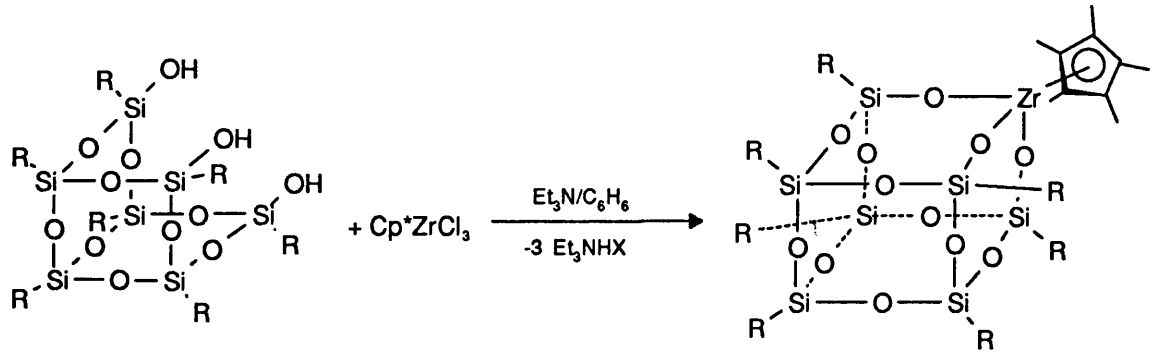
of $RSiCl_3$ monomers has already been discussed (section 1.2.2.A) and this section deals entirely with the strategies adopted in synthesising metallasilsesquioxanes. Three techniques are extensively utilised and are illustrated in scheme 8.



Scheme 8 Synthesis of metallasilsesquioxanes from POSS compounds

- Direct metathesis between the silanol and a less acidic alkyl, amide or alkoxide ligand. This route works well for electropositive metals (*e.g.* Zr, Ti, Al, Ga) and provides numerous interesting examples, *e.g.* $[(c\text{-}C_6H_{11})_7Si_7O_9(O_3W\{NMe_2\}_3)]$,[142] $[(c\text{-}C_6H_{11})_7Si_7O_9(O_3L_n[THF]_n)]$ where L_n = Nd, Y,[143] and $[\{(c\text{-}C_6H_{11})Si_7O_{12})\}_2M_2]$ where M = Mo or W.[144] However this route is hindered by the limited availability of appropriate metal complexes and failure to metathesise the less reactive M-C bonds of the late transition metals.

- Amine assisted metathesis of metal-halide complexes (scheme 9). This method has proven to be the most effective route for the synthesis of heterosilsesquioxanes complexes. Trisilanol (**1**) has been capped by a variety of reagents including: $O{=}VCl_3$,[21] Cp^*ZrCl_3,[145] $CpTiCl_3$, $TiCl_3(NMe_3)_2$,[146] $VCl_3(NMe_3)_2$,[21b] $CrCl_3(NMe_3)_2$, $RSiCl_3$ (R= H, aryl, alkyl, Cl),[16b] $MeGeCl_3$, $RSnCl_3$ (R = Me, Ph),[147] PCl_3,[148] $AsCl_3$, $SbCl_3$, BI_3,[149] $AlCl_3$,[150] $GaCl_3$ and GaI_3.



Scheme 9 Capping the corner of Fehers trisilanol

Problems arise when the potential capping moiety functions as an effective leaving group, thus in high valent L_nMX complexes, *i.e.* MoO_2Cl_2 or CrO_2Cl_2 the base-assisted cyclodehydration of the

silsesquioxanes occurs as common side-reaction.[138] This problem may be circumvented by capping the silsesquioxanes with a lower valent heteroatom and then oxidising the isolated moiety.

- Metathetic replacement of M-halide bonds by silsesquioxane anion equivalents is commonly used for the synthesis of siloxides from relatively unreactive late transition metal halides. Initial attempts at producing anionic silsesquioxane equivalents using sodium salts failed due to the unstable nature of the resultant silsesquioxane framework. However it was found that the softer anionic nature of tetraalkylstibonium salts did not promote skeletal rearrangements. Thus these entities can often function effectively as latent sources of silsesquioxanes anions, offering enhanced reactivity in comparison to the silanol.[151] Unfortunately their propensity to decompose in the presence of high-valent electrophilic metal halide complexes means their utility remains limited. This problem may be overcome using thallium(I) stabilised silsesquioxanes anions which are easily prepared *in situ* and give isolable metallasilsesquioxanes in high yield under reaction with MoO_2Cl_2 and CrO_2Cl_2.[152]

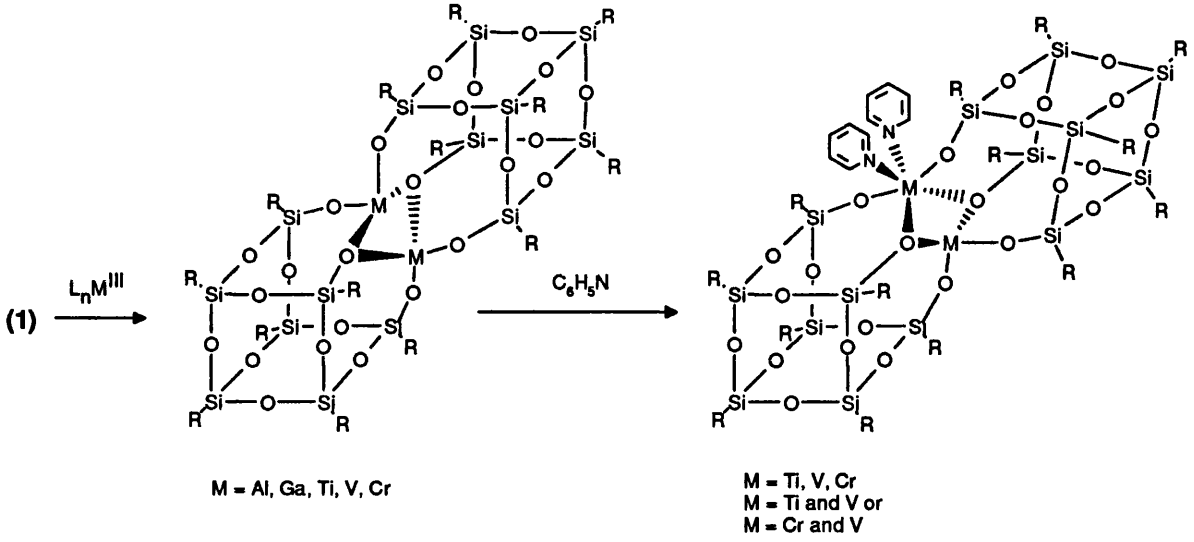
Reaction of silsesquioxanes with $SbMe_5$ or Me_3SiCl (in the presence of NEt_3) also answers pertinent questions regarding the relationship between the acidity of a silanol and the degree of H-bonding within the species. Trisilanol (**1**) is more reactive than other POSS compounds with less than 3 mutually H-bonded siloxyl groups, an observation that is supported in the faster reaction of a 1:1 trisilanol-$SbMe_5$ (or Me_3SiCl) mixture to yield only the monosubstituted product. Subsequent replacement of a second, and eventually a third, siloxy group by a $SbMe_4$ (or Me_3Si) moiety proceed at vastly reduced rates. The implications of this are that more extensive H-bonded silica surface sites are both more acidic and reactive towards a variety of reagents than less extensively H-bonded surface sites (*e.g.* isolated monosilanols and both vicinally and geminally H-bonded disilanols).[21, 151]

A final, and little used route involves the direct reaction of the POSS compound with the metal species. Only three compounds, $[(Si_8O_{12}H_6)\{Co(CO)_2\}_2]$,[153] $[HOs_3(CO)_{10}\{(\mu\text{-}O)Si_7O_{10}(c\text{-}C_6H_{11})_7\}]$,[154] $[(c\text{-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)CrO_2]$[155] have been isolated *via* this proceedure. All adopt monomeric configurations and provide interesting insights into the reaction chemistry of transition metal carbonyl-, and ester- silsesquioxanes.

(iii) Structural Features

The flexible nature of the Si-O-Si backbone enables the accommodation of a diverse array of metal and non metallic fragments in "capping the corner" of POSS compounds, in particular trisilanol (**1**). Whilst this is useful in binding a range of fragments, the high flexibility has thwarted attempts to produce low and usual co-ordination geometry, reactive species as dimerisation of the monomers oc-

curs (scheme 10). These circumstances do however provide an opportunity to produce mixed metal dimers through a combination of monomers.[21b]



Scheme 10 Dimerisation of transition metal silsesquioxanes

Structural characterisation confirms the propensity of many metallasilsesquioxanes to dimerise whilst solution studies of POSS compounds reveal dynamic behaviour through fluxion of the molecule, and the formation of equilibrium mixtures of monomers and dimers. Addition of π-donor ligands, such Ph_3PO or Me_3NO often leads to the equilibrium mixtures preferentially stabilising the monomer form.[21a, 156]

Analysis of x-ray structural data has been ostensibly used to establish the nature of the metal-ligand bonding interactions in metallasilsesquioxane compounds. Whilst M-O bond lengths provide a good indication of the degree of O($p\pi$)→M($d\pi$) interactions, the other nominal indicator, that of Si-O-M bond angle, is overridden by the geometric considerations imposed by the size of the capping metal species. Again it is often found that there is little correlation between M-O bond lengths and Si-O-M bond angles. The data indicate predominantly longer M-O bond lengths in POMSS compounds than those observed in simple alkoxide and siloxide species, which is consistent with a diminished capacity for O($p\pi$)→M($d\pi$) donation. This effect is also corroborated by the increased M-L interactions of competitive π-donors, and in summary it would be fair to say that POSS ligands do not produce electron rich complexes when compared to simpler model ligands.

(iv) Catalytic Activity

Metallasilsesquioxanes have provided a useful tool in the elucidation and understanding of key effects in the co-ordination polymerisation of ethylene on silica supported vanadate and chromate ester catalysts. Despite the huge amounts of research expended on these commercially important processes

the active intermediates, their formation, function and decay remain highly controversial. Modelling of homogeneous processes using both simple siloxide and POMSS compounds has been undertaken and their activity as pre-catalysts in the presence of $AlMe_3$ evaluated. Under identical conditions the relatively electron poor vanadate-silsesquioxane proved to be a highly effective catalyst for the formation of linear, high-density polyethylene, whilst the comparatively electron rich $[V{=}O(Ph_3SiO)_3]$ or $[CrO_2(Ph_3SiO)_2]$ compounds showed little or no activity.[95] Thus these mechanistic investigations of the POMSS/$AlMe_3$ system reveal that the electron donating nature of the ligand is crucial in determining the ability of the metal centre to act as a catalyst.

More recent work indicates that organometallic gels containing large amounts of active metal centres may function as highly effective catalysts. To this end Feher *et al.*[157] have developed nonchelating, phosphine-substituted silsesquioxane frameworks as rigid spacers to connect phosphine complexes of late transition metals. These exciting compounds, intially containing $[Rh(CO)_2Cl]_2$ moieties, offer the chemical selectivity of homogeneous catalysts with the engineering benefits of heterogeneous catalysts.

C. APPLICATIONS OF HETEROSILOXIDES IN MATERIALS SCIENCE

A very cursory inspection of recent literature reveals that thin solid films are becoming increasingly important in various technologies, including electronics, optics, solar energy, protective coatings and even temperature control of objects in space.[158] The diverse array of films deposited and their applications include, doped SnO_2 and TiO_2 films for optical coatings used to control reflection, transmission and absorption in transparent substrates, electronic devices produced from both Si, GaAs, CdTe semi-conducting, and $YBa_2Cu_3O_{7-x}$, $La_{2-x}Sr_xCuO_{4-y}$ superconducting films, electrochromic (WO_3) as well as abrasion and corrosion resistant films (SiC and TiN), all on many different substrates.[159]

Of the many methods available for the deposition of thin films, the two that have found widespread industrial favour are chemical vapour deposition (CVD) and sol-gel techniques.[160] Both technologies offer the opportunity to produce coatings which show excellent conformality and intregrity, prove highly adhesive to the substrate and may be reliably reproduced on a large scale.

CVD techniques are based on the formation of a thin solid film on a substrate by means of a chemical reaction in the gas or vapour phase. Reaction of the precursor(s) may be achieved by an array of methods, *e.g.* thermally, photochemically or in a plasma, with the properties of the resulting film being heavily influenced by the deposition conditions, the chemical nature and stoichiometries of the precursor(s) involved. Primary control over the deposition process is exerted by the precursor, which

ideally should exhibit high volatility, relative stablity towards polymerisation but react readily to form films of high purity.

Mechanisms of sol-gel processes are more easily identified and controlled than the gas phase CVD processes, due mainly to the reduced dynamic nature and complexity of the solution based technique.[161] As a result sol-gel processes require less equipment, are less expensive than CVD techniques, and enable a more complete tailoring of the precursor substrate. Film deposition is based upon the hydrolysis of colloidal suspensions, often consisting of metal-organic precursor moieties. Under these conditions, compounds such as alkoxides or alkyls build up a gel in which the partially hydrolysed compounds are linked together to form macromolecules. Removal of the solvent by evaporation affords very hard and porous aggregates (xerogels) suitable for powder product, whilst supercritically heating the gel results in loosely packed skeletons (aerogels). Development of the latter process, *e.g.* prevention of full gelation of the whole batch by using polymeric metal-organic intermediates and decomposing them pyrolytically leads to useful mono- (ZrO_2 and Al_2O_3) and multiphase (spinels) powders of high purity. The many useful end applications include catalyst supports, absorbants, reinforcing agents for plastics and insulators in microelectronics.

However whilst the two deposition processes appear greatly different from each other, three mutual problems exist:

- aggregation of precursor molecules
- rigorous control of impurities
- variation in film stoichiometry

These problems had been encountered in semi-conductor coating technologies utilised by the microelectronics industry, and had led to a concerted strategy involving both precusor design and process control. Improvements in both the performance of the coatings and relaxation of process conditions were demonstrated by tailoring precursors with facile ease of transport and decomposition (fragmentation behaviour). Thus whilst a great deal of research involving metal-heterosiloxide/siloxane compounds is orientated towards a greater understanding of catalytic processes a sizeable minority of studies are concerned with the synthesis of new precursors for the deposition of thin metal(oxide) or ceramic films by either technique.

This can be exemplified by examining the historical approaches utilised in the production of thin films of alumina and aluminosilicates. Initially the lack of volatile metal-organic precursors precluded attempts at producing alumina thin films by CVD and obliged deposition *via* a complex and unreliable sol-gel method. The process involving a two phase system consisting of aluminium hydroxide or oxide, mixed with an aqueous/organic solvent phase, was hindered by the strong

interactions of the precipitated gel with the precursor material. As a result it was extremely difficult to consistently prepare pure gels.[109d] These problems were circumvented by refining Ebelmans first unwitting production of a gel from a metal alkoxide.[162] In particular silica gels were successfully generated from the hydrolysis of silicon esters, principally tetra-ethylorthosilicate (TEOS, $Si[OC_2H_5]_4$). These gels were in turn superseded by the first, and superior, alumina gels generated from aluminium alkoxides, as reported by Adkins in 1922.[163] It was not however until the 1970s that the first aerogels were produced,[164] and the final step leading to the production of ceramic materials, that of sintering, was only completed in the 1980s by Yoldas.[165]

$$Al(OR)_3 \xrightarrow{H_2O} Al\ gel \xrightarrow{Heat} Al_2O_3$$

In contrast to these enormous advances in the control of the deposition processes, the choice of precursor and synthetic methodology remained limited. Consequently the drive to produce a greater range of coatings was hindered by the weak link in the deposition sequence, that of the problems inherent with the hydrolysis of aluminium alkoxides systems. The implementation of detailed mechanistic and synthetic strategys led, initially, to the discovery that bridging alkoxy moieties were proving to be more resistant to hydrolysis than associated solvent molecules, and under some conditions more stable than terminal ligands.[161] Thus aggregation was having a greatly adverse effect on the hydrolysis reaction kinetics as well as lowering the volatility of the materials and hence their potential utility as CVD precursors. Despite this, homogeneous aluminosilicate films of $(Al_2O_3)_x(SiO_2)_y$ were reported to have been deposited by MOCVD using $[Al(OSiEt_3)_2]_2$ as a precursor.[166] Increasing the bulk of the attached alkoxide (or siloxide), reduced oligomerisation[167] and so improved the volatility and hydrolysis rates of the precursor, although the problems were not significantly reduced until Yoldas synthesised the first mixed siloxide/alkoxide compounds, $[Al(OSiR_3)_n(OR')_{3-n}]$.[168] Of particular interest was $[Al(OSiEt_3)(O^nBu)_2]$[169] which proved to be useful single source precursor for aluminosilicate materials.

$$Al(OSiR_3)_n(OR')_{3-n} \xrightarrow{H_2O} Al-Si\ gel \xrightarrow{Heat} (Al_2O_3)_x(SiO)_y$$

However one major disadvantage of using these siloxide complexes as precursors was the comparable rates of hydrolysis for the aluminium siloxide, $[R_3SiO]^-$ and alkoxide, $[RO]^-$, groups. Accordingly control over the Si:Al ratio in the resulting alumoxane was difficult to obtain, with deleterious consequences for the ceramic subsequently produced. Futhermore a high proportion of the siloxide was lost as silanol during hydrolysis which made the route economically unattractive. Further tailoring of the precursor was undertaken to overcome this problem. Organometallic materials incorporating alkyl ligands in combination with siloxide functions *e.g.* $[Me_2Al(OSiMe_2R)]_2$ where R = akyl or phenyl were produced.[109e] The rate of hydrolysis of the alkyl functions greatly exceeded that of the siloxide

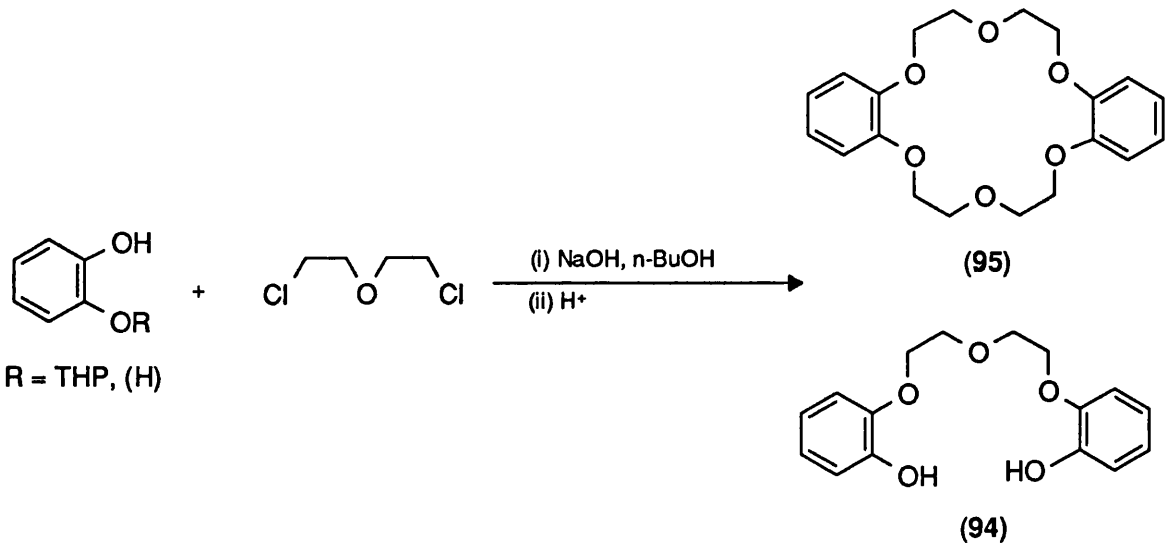
ligands and thus minimised the loss of siloxide and increased control of the Si:Al ratio result. As a result enhanced reactivity and volatility as well as cleaner decomposition mechanisms have been witnessed in a new generation of compounds. These include dimethylsiloxy-aluminium dihalides, $[Me_2HSiOAlX_2]_2$ where X = Cl, Br[170] which offer themselves as exciting new precursors for film formation.

1.4 OXA- AND AZA- CROWN ETHERS

1.4.1 INTRODUCTION

The existance of macrocyclic compounds closely related to crown ethers had been well established in the literature many years before the remarkable explosion of interest in these compounds. Cyclic polyethers, derived from a variety of reagents, had been documented by Lüttringhaus, Ziegler, Adams, Whitehill, and Sichert-Modrow in the 1930s and 40s. In the late 1950s Stewart, Wilkinson and Colclough reported cyclic tetrameric species derived from the transition metal catalysed polymerizations of ethylene- and propylene oxide.[171] Indeed Wilkinson noted the ability of the cyclic tetramer of propylene oxide to dissolve trace amounts of metallic potassium and sodium-potassium alloy to give an unidentified, unstable blue solution. These cylic oligomers are now broadly classified as heterocylic crown ethers.

Nevertheless the discovery of crown ether compounds is attributed to Pederson in 1967,[172] due mainly for his recognition of their complexing ability and descriptions of specific characteristics.[173] As with many significant discoveries in chemistry, the initial isolation and characterisation of a species owes much to serendipity, but its existence revolutionises an area of science.



Scheme 11 Pedersons initial synthesis of dibenzo-18-crown-6

Thus Pederson, in attempting to synthesise [(2-hydroxyphenoxy)ethyl]ether (**94**) by reaction of a tetrahydropyrane protected catechol with dichloroethyl ether, isolated white fiborous crystals of dibenzo-18-crown-6 (**95**) in 45% yield. This by-product, produced initially in very low yield, laid the foundations for the vast range of crown ethers known today.

These simple, first generation crown ethers were subsequently followed by analogues possessing nitrogen and suphur donor atoms. Monocylic ligands, were in turn, superseded by bicyclic compounds such as Lehns' cryptands and cavitands.[171] Design of these macrocycles through the strategic positioning of additional binding sites or steric barriers near the cavity of the crown ether enabled the ligand to function as a shape selective template or mimic enzyme systems.

The modern definition of a crown ether has not yet been strictly delineated but they can be generally described as "macrocyclic compounds having hetero atoms such as O, N, S as the electron donor atoms in their ring structures, and the property of incorporating cations into their cavities."

1.4.2 SYNTHESIS OF CROWN MACROCYCLES

A. CLASSIFICATION AND NOMENCLATURE

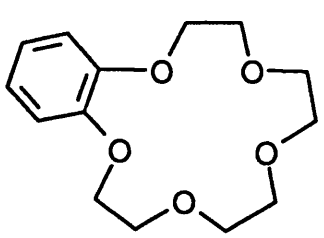
The macrocylic polyethers synthesised by Pederson were named by reference to their chemical structure and the shape of the complex formed upon enclosure of a metal ion in the cavity of the crown. Macrocyclic polyethers containing only oxygen as the donor atoms are known as crown ethers. Substitution of some O atoms for N donors (NH, NR) gives cyclic amino ethers known as azacrown ethers, their direct sulphur analogues are called thiacrown ethers. Macrocyclic compounds containing only N atoms are termed azacrowns, and macrocyclic polysulphides having only S atoms are labelled thiacrowns.

The strict IUPAC nomenclature gives rise to long, complicated names which are often abandoned in favour of Pedersons convienent system. The general rules are: for crown ethers having an aromatic or cyclohexyl ring, the crown names consist of:

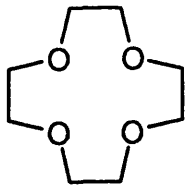
- the kind and number of the group substituted in the polyether ring
- the total number of atoms which constitute the crown ring (corresponding to the cavity size)
- the term crown
- the number of O donor atoms, that is, the ether linkage in the crown ring combined with hypens

This can be exemplified by 15-benzo-crown-5 (**96**) and dibenzo-18-crown-6 (**95**). For crown ethers without any substituted groups, the crown names consist of [the total number of atoms which constitute the crown ring]-[crown]-[number of O donor atoms], thus for example 18-crown-6 (**97**). These

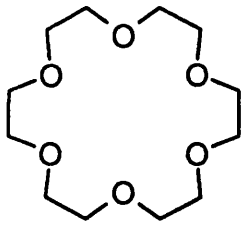
rules are not definitive but provide a convienent means to represent simple and symmetrical crown ethers.



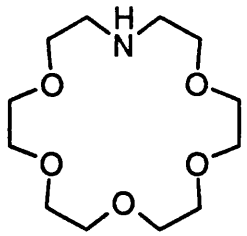
15-benzo-crown-5



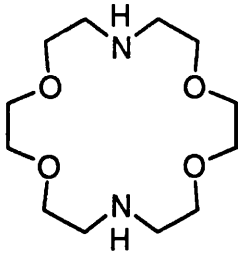
12-crown-4



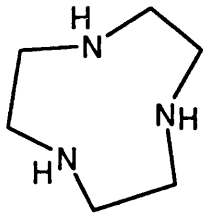
18-crown-6



1-aza-18-crown-6



7,16-diaza-18-crown-6



1,4,7-triaza-cyclononane

Figure 22 Structural formulas and nomenclature of typical crown ethers

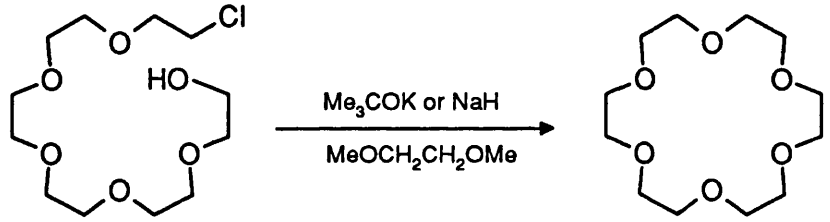
A similar approach could be adopted in the case of aza- and thia- crown ethers but the need to express the position of the heteroatom ensures the use of IUPAC nomenclature. Thus we have 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (1-aza-18-crown-6) (98) and 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (7,16-diaza-18-crown-6) (99) which are often shortend to monoazacrown and diazacrown ether.

B. PREPARATION OF CROWN ETHER MACROCYCLES

There are a great variety of methods for producing crown compounds but, in all the paramount concern is the minimalisation of the competing side reaction leading to the production of linear polymers. In general, the Williamson synthesis and other basic reactions for the generation of ethers are utilised in the assembly of crown ether compounds in which synthetically attractive yields of polyether macrocycles are facilitated by a cationic presence operating as a templating agent during the ring closing step. Thus Pederson attributed the cause of the improved yields of crown (95) to be "the ring-closing step, either by a second molecule of catechol or a second molecule of *bis*(2-chloroethyl)ether, was facilitated by the sodium ion which, by ion-dipole interaction wrapped the three-molecule intermediates around itself in a three-quarter circle and disposed them to ring closure".

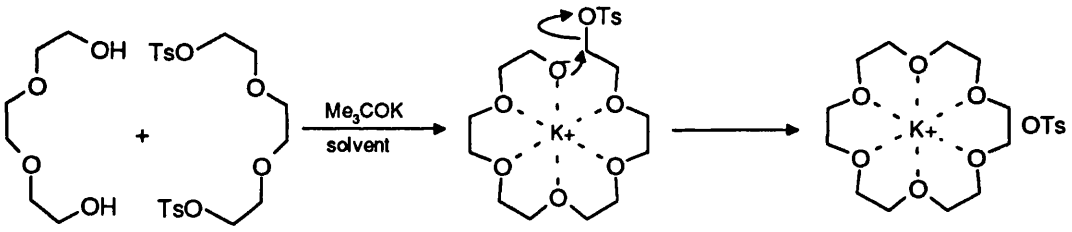
Templating effects may be broadly divided into three types.[185] The first type, that of the thermodynamic templating effect, promotes macrocycle formation by removing the product from the reaction as a macrocycle metal complex. Secondly, the equilibrium template effect, in which the reactants take part in a reversible reaction to give an intermediate that forms a stable complex with the metal. All reactants then proceed to a macrocycle-metal complex. An important difference between the two phenomena is that in reactions involving the thermodynamic effect different products are obtained for the metal-assissted and metal-free reactions, but in reactions involving the latter, the same products are produced by the two reactions. The final mode is the kinetic templating effect and is defined as providing a route to the product, *via* the co-ordinating actions of the metal on the reactants, which would not be available in the absence of the metal cation.

Evidence of templating effects may be percieved from collating the published proceedures for the preparation of 18-crown-6 (**97**), see table 16.[171] Pedersons first reported synthesis of (**97**), *via* the base-promoted cyclisation of hexaethyleneglycol monochloride in $MeOCH_2CH_2OMe$ using either Me_3COK or NaH as base, suprisingly gave low yields (2%) of isolated product (reaction 1.14).[172b]



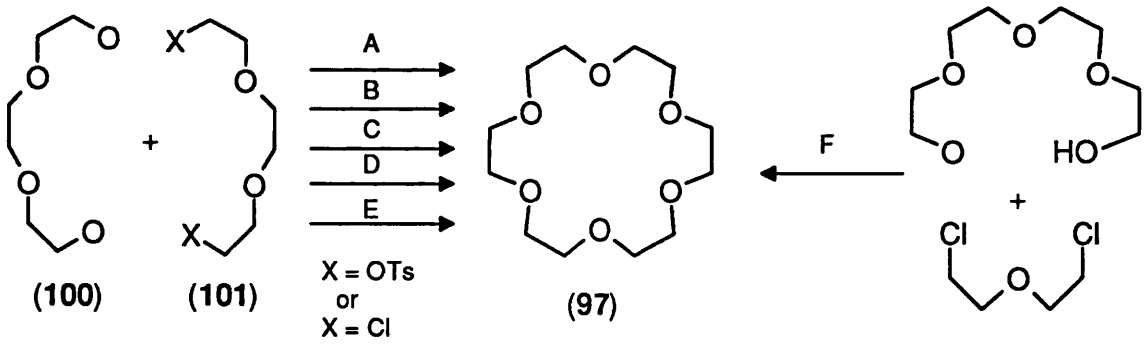
1.14

Subsequently improved yields (33-93%) were reported from reaction of triethyleneglycol with its di-tosylate in the presence of Me_3COK (reaction 1.15),[174] from triethyleneglycol plus its dichloride, with KOH in aqueous THF[175] or from tetraethyleneglycol, diethyleneglycol dichloride, and KOH in dry THF (yields 30-60%).[176]



1.15

In all these cases, a templating effect involving the K^+ ion is an attractive proposition, at least as a partial explanation for the high yields.



Method	X	Base	Solvent	Yield (%)
A	OTs	Me_3COK	Me_3COH/C_6H_6	33
B	OTs	Me_3COK	THF	30-60
C	OTs	Me_3COK	DMSO	84
D	OTs	Me_3COK	DME	93
E	Cl	KOH	THF/H_2O	40-60
F	Cl	KOH	THF	30

Table 16 The syntheses of 18-crown-6

The existance of acylic intermediates in reactions of **(100)** with **(101)** *via* methods B-D has been confirmed by the following observations

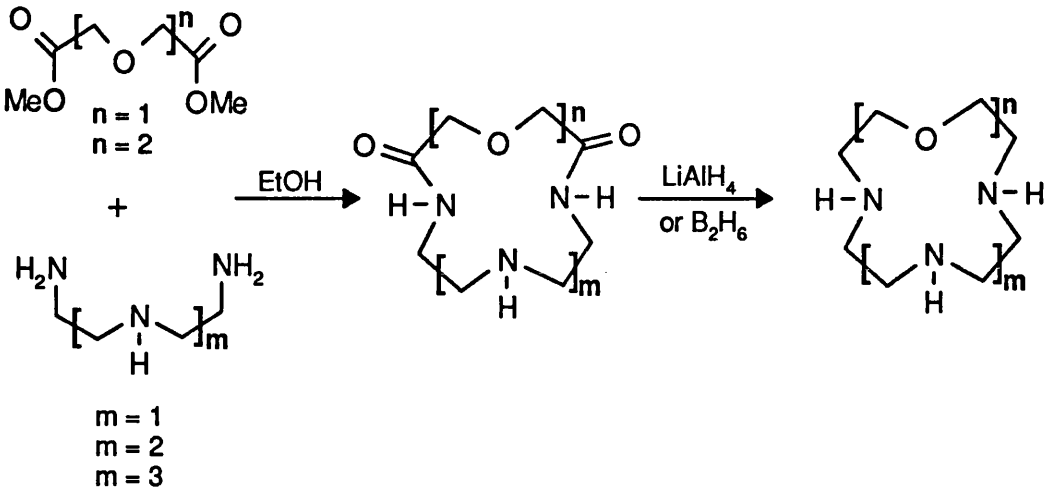
- the macrocycle **(97)** can be isolated as its potassium tosylate intermediate
- doubling the concentration of reactants in method C results only in a decrease in the yield from 84 to 75%
- when tetra-*n*-butylammonium hydroxide was used as the base the yield of **(97)** was drastically reduced

All these observations support the existence of a templating effect which often operates under optimal conditions when the diameter of the cation corresponds closely with the cavity diameter of the macrocycle being formed. However this is not always the case and the necessity of introducing a specifically sized cation has yet to be proven. Reinhoudt has also demonstrated the effectiveness of the templating species is moderated by the environment in which it is employed.[177] Thus for the syntheses of crown ethers the choice of solvent, the nature of reactive groups on the organic substrates, the size/charge ratio of the templating ion, its counterion, as well as the use of high dilution conditions are influential in determining yields.

C. SYNTHESIS OF AZA CROWN ETHER MACROCYCLES

The large number of synthetic methods available for the production of azacrown ethers can only be appreciated by considering the immense variety and number of macrocycles synthesised to date.[171,

[178] Many cryptands have been produced by Lehn[179] and these are not reviewed here. Cyclisation of dimethyl esters of α,ω-dicarboxylic acids with polyethylenepolyamines in refluxing ethanol provides a convenient experimental route for producing moderate yields of many crowns under conditions not requiring high dilution (reaction 1.16).[180]

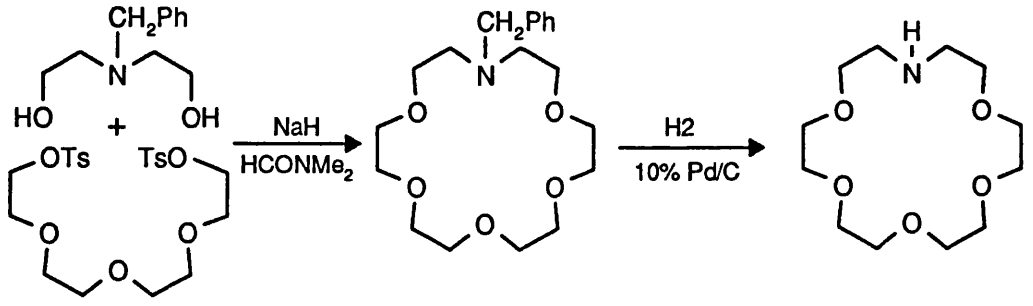


1.16

	n	m	Yield (%)
(106)	1	2	12
(107)	1	3	12
(108)	2	1	32
(109)	2	2	67

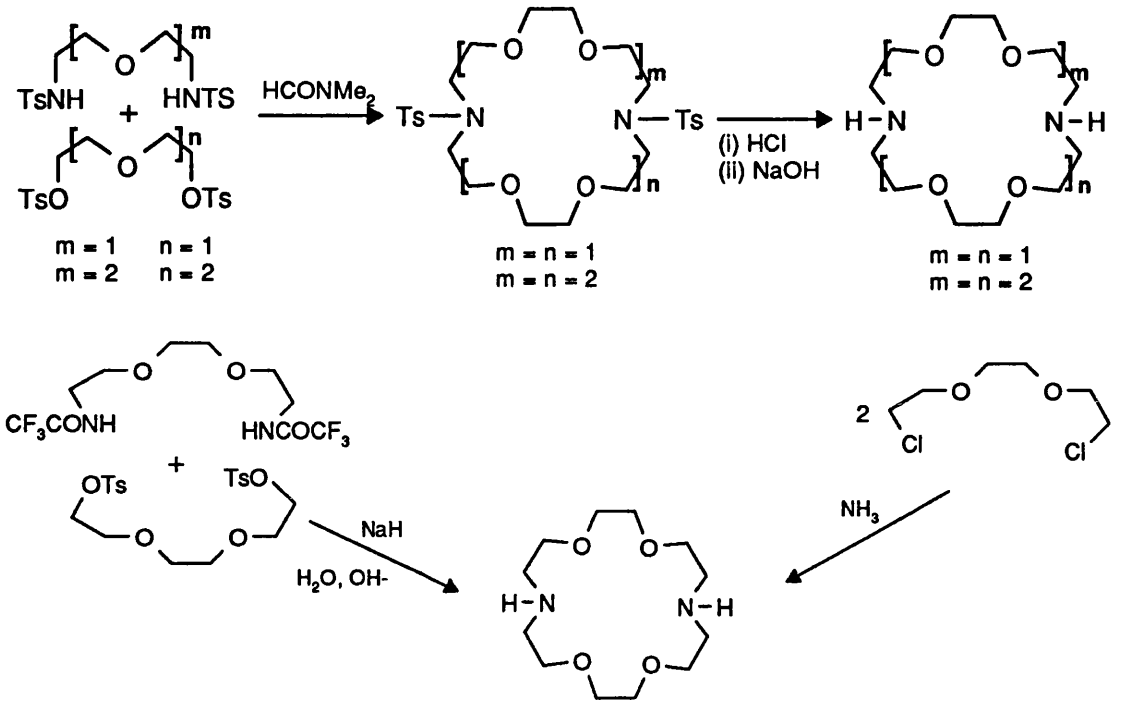
	n	m
(102)	1	2
(103)	1	3
(104)	2	1
(105)	2	2

Other methods include reaction of a glycol, such as tetraethylene glycol and *N*-benzyldiethanolamine to give monoaza-18-crown-6 (**98**), reaction 1.17.[181]



1.17

Diaza-12-crown-4 and diaza-18-crown-6 (**99**) derivatives have been prepared in high yield by reaction of the appropriate dianions of α,ω-bis-sulphonamides with diethyleneglycol ditosylate and triethyleneglycol ditosylate respectively.[182] The corresponding free amines are obtained by acid-catalysed hydrolysis of the cyclic bis-sulphonamides followed by treatment of the salts with base (scheme 12).



Scheme 12 A typical synthesis of aza crown ethers

Lower yields of (**99**) are obtained from the reaction of triethyleneglycol ditosylate with the α,ω-bistrifluoroacetimide dianion followed by alkaline hydrolysis, or *via* the reaction of two equivalents of α,ω-dichloride with excess NH_3.[183]

1.4.3 CROWNS AS COMPLEXING AGENTS

A. INTRODUCTION

Pedersons' observation that the addition of NaOH to a mixture of dibenzo-18-crown-6 in methanol vastly improved the solubility of the macrocyclic polyether provided the initial impetus for an investigation of the properties of crowns. Reactions with alkali and alkaline earth metals in organic solvents were used by Pederson to characterise crown ethers.

"The most striking characteristic of crown ethers was their ability to form stable complexes. During complexation, the cation portion of a metal salt, ammonium salt, or organic compound (guest) is bound by a crown compound (host) bearing donor atoms such as O, N, S."

The complexation ability of a crown compound and the stability of the resulting complex depend to some degree on the relative sizes of the diameter of the cavity in the crown compound and the diameter of the cation. They are also greatly influenced by the charge and 'hardness' of the cation, as well as by the kinds of donor atoms present in the crown compound, which determines 'hardness' and basicity. Futhermore, complexes may exhibit enhanced solubility in various organic solvents, includ-

ing non-polar solvents, because crown compounds have hydrophobic groups.[171] The degree of complexation is also extremely dependent upon the medium in which the components are dissolved. For example metal guest cations often retain some of their solvation shell of water molecules upon complexation with crown ethers from aqueous solution.[184,185]

Examination of complexes of simple inorganic cations with crown-ethers conclude that they are held together by ion-dipole interactions between the cation and the negatively charged O atoms on the polyether ring. Structural analyses confirm that where possible the cation is held inside the cavity of the crown ether by the inwardly directed lone pairs of electrons belonging to the O atoms. Figure 23 shows the central position, equidistant from each O atom, of the cation in crown ether complexes. This regular arrangement of donor ligands confers an entropic advantage over other synthetic host molecules.

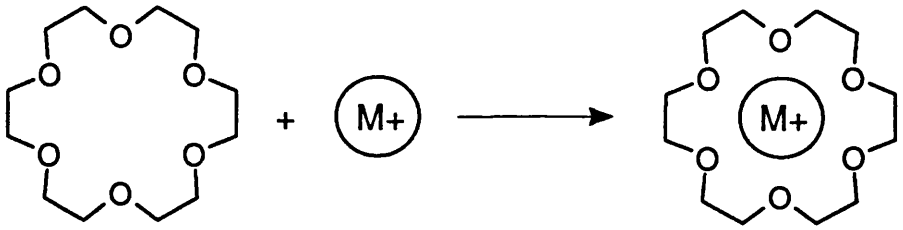
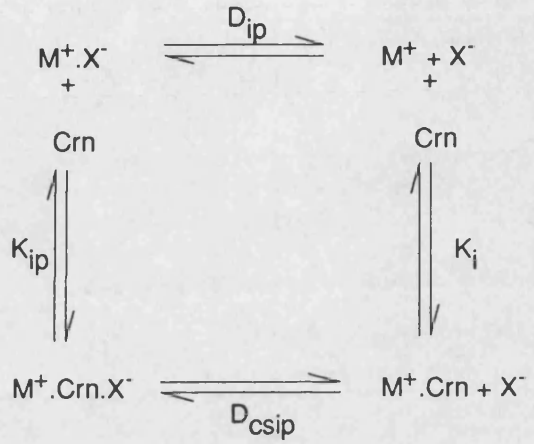


Figure 23 The positioning of a cation in a crown ether macrocycle

The complexation ability of crown ethers provides an interesting comparison with the solubilising and stabilisation effects of polar aprotic solvents employed in Grignard reactions, living polymerisations and reactions proceeding *via* nucleophilic substitution. Cyclic ethers such as 1,4-dioxane, THF, linear polyethers; the glymes, *e.g.* 1,2-dimethoxyethane and diethylene glycol dimethyl ether as well as dipolar solvents such as DMSO and DMF have been found to be excellent solvents for these reactions involving charged intermediates. Reactions are assisted, in the first two examples, by stabilisation of cationic intermediates *via* the linkage of the lone pair of electrons from the O atom of the ether to the cation. In the latter example, stabilisation occurs because of the solvents capacity for inducing ionisation. In most cases, the stabilisation of the cation produces a more reactive anion which generally increases the rate of reaction. Crown ethers function as better "anion activators" (and hence "cation deactivators") because of their greater ability, in comparison with the solvents, to complex with the cation.

B. STABILITY AND SELECTIVITY TOWARDS INORGANIC CATIONS

A measure of the stability of the complex may be obtained from its association (K_i and K_{ip}), or dissociation (D_{ip} or D_{csip}) constants which can be determined by a variety of physiospectroscopic techniques. In a solution containing a crown ether (Crn) and a salt of a univalent cation (MX), the equilibria (scheme 13) can exist. D_{ip} and D_{scip} are the dissociation constants of the ion pair $M^+.X^-$ and the crown ether separated pair $M^+.Crn.X^-$ respectively. K_i and K_{ip} are the association constants of the free cation M^+ and the ion pair $M^+.X^-$ respectively with the crown ether.[186]



Since $K_{ip} \times D_{scip} = K_i \times D_{ip}$ the system can be described by three parameters. In polar solvents such as water and methanol, D_{ip} is very high for most salts, and consequently K_i is the only association constant of importance. In apolar solvents, on the other hand, one deals mainly with K_{ip}. There are a number of parameters which affect the stability of the host-guest pair:

- Cavity size and diameter. X-ray crystallography substantiates that the overriding factor is the ratio of cation to cavity size. For uni- or bi- valent cations a unitary value indicates the formation of the most stable complexes whilst deviation from the perfect fit results in a loss of binding capacity.

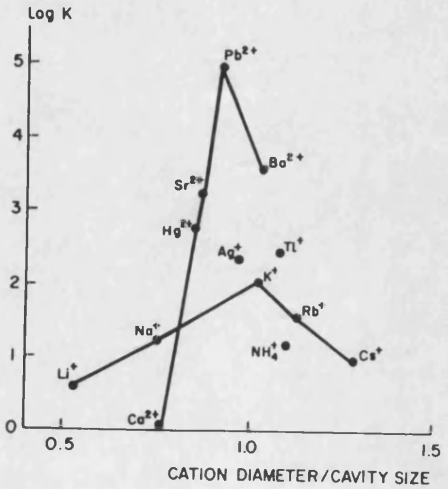


Figure 24 Relation between log K and the ratio of cation diameter to cavity size for dicyclohexyl-18-crown-6 in water at 25°C.[186]

- Conformational flexibility and rigidity. Ligands with small cavities are generally quite rigid, since a small cavity is delineated by short, relatively inflexible chains. Larger ligands, with larger cavities, are generally more flexible and undergo conformational changes. Thus cations considerably smaller than the cavity of the crown, can be accomodated. For example dibenzo-30-crown-10 can wrap around the K^+ cation so permitting the co-ordination of all 10 oxygen donors. In effect the crown reduces the size of the cavity to the size of the cation. If the cavity is too small to accommodate the cation, *e.g* K^+ and benzo-15-crown-5, 2:1 sandwhich type complexes may be formed.

- Donor atom number. A crown ether in a cation ion complex replicates the inner solvation sphere of a metal ion. For optimal stability the number of donor sites should be roughly equivalent to the preferred co-ordination number of the atom (often their co-ordination number when complexed with water molecules).

- Ring number and type. The overall macrocycle topology determines the manner in which the ligand and cation interact and defines the type of complex formed. Replacement of the cation co-ordination shell as completely as possible by an enveloping ligand results in the higher stability of the complex.

- Spatial arrangement of binding sites. The most effective binding is achieved if all the dipoles of all the donor atoms are directed towards the centre of the cavity. Any disruption to the number, direction and magnitude of these dipoles results in a reduction of the binding constants.

- Additional binding sites. The introduction of additional binding sites at strategic positions near the cavity of the crown allows the formation of three dimensional arrays of binding sites. Provided the additional ligating members are tailored to the cation this effect can substantially increase the binding constants and selectivity of a crown.

- Electron density at the binding sites. A reduction of the available electron density at the donor sites leads to a marked drop in binding capacity. This affect is achieved by replacing $-CH_2CH_2-$ unit(s) by groups demonstrating electron inductive effects. Thus the crown ether, hexabenzo-18-crown-6, contains O atoms conjugated with benzene rings and it displays reduced binding ability compared to 18-crown-6. Furthermore, replacement of the $-CH_2CH_2-$ unit(s) in a controlled manner can be utilised to enhance the selectivity of the crown.

- Heteroatom donor sites. Replacement of one or two O donors by N (or S) atoms results in a reduction in the ion-dipole interaction between the cation and the donor atom. *Ergo* the stability of the crown complexes with the alkali and alkaline metals is lessened. The softer donor properties of N and S atoms increase the complexation abilities of aza- (or thia-) crown ethers with softer

Lewis acids. Thus a vast range of transition and heavy metal complexes are formed with this class of crowns.

Crown ether			log *K*	
Type	A	B	K^+ in MeOH	Ag^+ in H_2O
I	O	O	6.1	1.6
II	O	O	5.0	-
II	NR	O	4.1	-
I	NH	O	3.9	3.3
II	NH	O	3.2	-
I	NH	NH	2.0	7.8
II	NH	NH	1.6	-
I	S	S	1.2	4.3

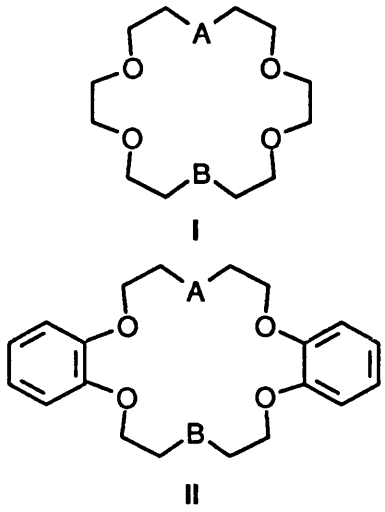


Table 17 Complexation abilities (log k) of crown ethers in which some of the O donors are replaced by N or S atoms[186]

1.4.4 STRUCTURES OF CROWN COMPLEXES

A. CRYSTAL STRUCTURES OF CROWN ETHER COMPLEXES

The structures of 1:1, 2:1, 3:2 and 1:2 cation/crown complexes have been determined for a wide variety of crown compounds by single crystal X-ray diffraction. Of all polyether macrocycles, the 18-crown-6 ligand has been the most comprehensively studied. This includes an increasing number of 18-crown-6 derivatives of polar organic substrates:

B. INTERACTION WITH ORGANIC GUEST MOLECULES

Neutral guest molecules containing proton-donating sites, *e.g.* acidic CH, NH or OH groups, readily form complexes with 18-crown-6. Complexes are stabilised by dipole-dipole or H-bonding interactions of the guest with the ether oxygens of the crown. When the guest molecule possesses only a single donor group almost invariably the stoichiometry of the complexes formed involves the binding of more than one guest moiety to a single host molecule. The guest molecules are generally found in X-ray determinations to be in a "perching position", lying above and below the ring, usually approaching the equivalent opposite sides of the macrcycle in a symmetric manner. If the guest contains two well spaced donor functions (>5 Å) then a complex of 1:1 stoichiometry may be formed. These compounds prevalently adopt a polymeric chain configuration in the crystal lattice. Representative examples are given in table 18.[171]

Of note are the complexes containing monodentate acidic OH groups, such as substituted phenols.[187] These moieties do not associate directly with 18-crown-6, but form complexes *via* water molecules, to which they have a high affinity, attached to the macrocycle ring (figure 49, page 108). The crystal structure of a binary hydrate complex of 18-crown-6 was recently published (figure 51, page 109).[188]

Guest compound	Host:guest ratio	Guest coordinating function
Nitromethane (110)	1:2	CH
Dimethyl sulphate (111)	1:1	CH
2,4-Dinitroaniline (112)	1:2	NH
***m*-Nitroaniline (113)**	1:1	NH
Formamide (114)	1:2	NH
***p*-Nitroaniline (115)**	1:2	NH
Urea (116)	1:5	NH
Thiourea (117)	1:4	NH
Thiourea (118)	1:2	NH
Cyanamide (119)	1:2	NH
***N,N'*-Dimethylthiourea (120)**	1:2	NH, CH
***N*-Methylthiourea (121)**	1:1	NH, CH
4,4'-Biphenyldiol·2H_2O (122)	1:1	OH
2,4-Dinitrophenol·H_2O (123)	1:2	OH
3-Nitrophenol·H_2O (124)	1:2	OH
Cyanoacetic acid·H_2O (125)	1:1	OH, CH

Table 18 Molecular complexes of 18-crown-6 with neutral guests

Aza-crown ethers provide an interesting structural subset of macrocycles as they possess one or more basic NR (R = H, alkyl) functions in comparison to crown ethers. The structure of diaza-18-crown-6, in its uncoordinated state, is stabilised by the two inwardly-turning amine hydrogen atoms which fill the cavity between the four centrally located lone pairs of the ring oxygens.

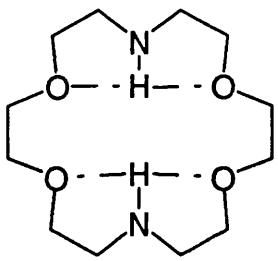


Figure 25 Uncomplexed diazacrown ether

These weak intramolecular N-H···O interactions are easily distorted upon the formation of even weak complexes with neutral substrates. On complexation with metal cations the relative orientation of the hydrogen atoms on N is inverted; the hydrogen atoms now point outward while the nitrogen lone pairs are directed towards the centred cation.

Protonation of aza-crown ethers allows complexation with either neutral molecules or with anions. Protonation of both nitrogen atoms is observed in the 2:1 complex formed with HNO_3 and diaza-18-crown-6.[171] A similar effect can be observed in the 1:1:1 complex of monoaza-18-crown-6·H_2O·HCl (see figure 51)[189] and complex H-bonding arrangements are also witnessed in the protonated complexes of pyrido-crown ethers encountered in strongly acidic media. In these cases the positive charge is mainly situated on the ligand rather than the guest.[190]

C. Co-ordination of Metal-Ligand Assemblies

Crowns interact with neutral or cationic transition species in a manner similar to that of small organic substrates. Crystal structures have been obtained for a variety of compounds, including the 1:2 complex between 18-crown-6 and *trans*-$[Ir(CO)(NCCH_3)_2(PPh_3)](PF)_6$] (**126**).[191] The metal moiety is co-ordinated to the crown through the acidic C-H bonds of the methyl groups from the two iridium bound acetonitriles. The methyl groups are situated at opposite sides of the crown (3.24-3.38 Å) from the ring. A 1:2 complex with *trans*-$[PtCl_2(PMe_3)(NH_3)]$ (**127**) has also been characterised.[192] The platinum entities are bound to opposite faces of the crown *via* the amine H-bonding interactions with all six oxygens of ring (N-O distances 3.04-3.31 Å).

The inclusion of water in transition metal-crown complexes has been documented. In some cases, it does not participate in H-bonding to the crown, *i.e.* $[Cu(NH_3)_3(H_2O)](PF)_6$ (**128**)[193] but in others the crown moiety is *via* the co-ordinated water in the metal complex or cation (see table 19).

D. Adducts with Charged Guests

Binding of guest molecules containing charged (or partially charged) non spherical entities significantly alters the electrostatic balance of the complex. On the whole, crown ethers form more stable complexes with cations than with neutral molecules because of the electronegative potential in the cavity of the macrocycle (table 19). This factor may be somewhat offset by the electrostatic repulsions of the cations if the complex contains two large guests to a single host which are generally situated at opposite sides of the crown.[194]

Guest compound	Host:guest ratio	Guest coordinating function
$Ph_3PCH_3 \cdot PF_6$ (129)	1:2	CH
Hydroxylammonium perchlorate (130)	1:1	NH
Amminetrifluoroboron (131)	1:1	NH
Toluenediazonium·BF_4 (132)	1:1	N≡O
Phenyldiazonium·PF_6 (133)	1:1	N≡O
Hydronium perchlorate (134)	1:1	OH
Hydronium chloride (135)	1:1	OH
$[WOCl_5] \cdot H_5O_2$ (136)[a]	1:1	OH
$[K^+(18\text{-crown-6})Cr(CO)_5Cl]$ (137)[195]	1:1	K^+
$[W(CO)_4Cl_3] \cdot H_3O^+$ (138)	1:1	OH

a Complex with 21-crown-7, also 18-crown-6 with H_3O^+

Table 19 Molecular complexes of 18-crown-6 with charged guests[171]

1.4.5 APPLICATIONS OF CROWN COMPOUNDS

Applications of crown ethers are most convientently classified according to the functions derived from their specific characteristics of these some are briefly noted below:

(i) Applications of the crown for selective capture, separation and transport of cation. Some examples of this include:

- Separation of mixtures of alkali or alkaline earth metal ions such as Na^+-K^+, and Ca^{2+}-Sr^{2+}
- Capture, recovery, removal, separation or purification of heavy metals such as Ag^+, Cd^{2+}, Hg^{2+} and Pb^{2+}
- Ion transport membranes, including liquid membranes
- Transition metal complex catalysts
- Stabilisation of unstable anions

(ii) Applications of the capacity of the crowns to stabilise inorganic salts in organic solvents and for the activation of anions.

- Inorganic syntheses, such as the synthesis of metal carbonyl derivatives
- Employment in organic synthesis, with particular importance in their use as homogeneous organic reactions using inorganic salts; organic synthesis under mild conditions utilising "naked" anions and reactions with liquid-liquid or solid-liquid phase transfer catalysts.
- Anionic polymerisations utilising the solubilisation of alkali metals

Chapter Two: Molybdenum and Tungsten Siloxides and Siloxanes

2.1 SUMMARY

The focus of our research has been to extend the range and knowledge of high oxidation state oxo-tungsten moieties supported by hard, π-donating ancillary siloxide ligands. The alkali metal silanolates such as R_3SiOM (M = Li, Na, K; R = Me, Ph) and $[Ph_2SiONa]_2O$ and the strained ring hexaphenylcyclotrisiloxane were reacted with tungsten hexachloride and oxo-chloride species to yield an array of air sensitive compounds.

The addition of sodium triphenylsilanolate to a suspension of $[W(O)Cl_4]$ gave only the *tris*-substituted product $[W(O)Cl(OSiPh_3)_3]$ independent of reactant stoichiometry. The same silanolate reacted with $[W(O)_2Cl_2(TMSO)_2]$ to produce $[W(O)_2(OSiPh_3)_2(TMSO)_2]$. However attempts to generate DMSO and Ph_3PO analogues resulted in the unexpected isolation of dinuclear species $[W(O)_2(\mu\text{-}OSiPh_3)L]_2$ (L = DMSO, $OPPh_3$) containing bridging siloxide ligands.

$[WO\{OSiPh_2O\}_2]$ was isolated upon the addition of a THF solution of $Ph_2Si(ONa)_2$ to a suspension of $[W(O)Cl_4]$. The disilanolate displays the expected bidentate-bridging behaviour across two metal centres. Addition of the longer chain disodium silanolate $[Ph_2SiONa]_2O$ to $[W(O)Cl_4]$ produced $[WO\{O(SiPh_2O)_2\}_2]$ which could not be completely purified.

Oxygen abstraction reactions of hexamethyldisiloxane in dichloromethane with tungsten hexachloride and tungsten oxychloride have been previously used to generate $[W(O)Cl_4]$ and $[W(O)_2Cl_2]$ respectively. Under identical conditions $[Ph_2SiO]_3$ reacted with WCl_6 to produce $[W(O)Cl_4]$ in similar yields to those of the bis(silyl)ether. A similar result was observed when the reaction was carried out in acetonitrile, however in THF solutions a gelatinous material which was identified as a ring opened THF polymer was formed.

In what can formally be described as a novel insertion reaction into a cyclosiloxane ring, a spirocyclic tungstasiloxane, $[WO\{O(SiPh_2O)_3\}_2 \cdot THF]$ was isolated in low yield and structurally characterised from the reaction of $[W(O)Cl_4]$ with $[Ph_2SiO]_3$. The larger octaphenyltetracyclosiloxane failed to react with $[W(O)Cl_4]$, which probably reflects the less strained nature of the siloxane ring.

Prelimary, but largely unsuccessful attempts to couple silanol and siloxane entities to the the binuclear $[Mo_2(O_2CCH_3)_4]$, $K_2[Mo_2Cl_8]$ moieties containing metal-metal quadruple bonds are described.

2.2 RESULTS & DISCUSSION

Transition metal siloxides and siloxanes can be produced from a wide array of precursors using any one of a variety of synthetic methodologies (see introduction). The most commonly utilised method, that of metal-halide metathesis involves the addition of an alkali metal silanolate to an etheral suspension of metal halide. The product may then be separated from the alkali metal salt (often sodium chloride) by extracting the mixture with a suitable non-polar organic solvent. However despite its widespread use, the route contains a number of inherent problems.

An alternative procedure, and one which is gaining popularity relies on the electronic nature of the metal to generate a heterosiloxide bond. Under favourable conditions oxophilic metal moieties may cleave the siloxane bond of silylethers or cyclosiloxanes to generate a heterosiloxane species. This methodology, which can also be used to produce early transition metal oxo-halide species, offers a potentially cleaner and simpler workup of products and is discussed later in the chapter.

2.2.1 PREPARATION OF SILANOLS AND SILOXANES

In assessing the electronic impact of supporting a catalytically active metal centre on a silica substrate, an array of silanol species that may act as potential models for a heterogeneous catalyst can be used. *Ergo* the synthesis of model complexes allows the investigation of different facets of the behaviour of silica by tailoring the denticity and the electronic nature of the appended organic functionality's of the model siloxane to replicate those of the solid substrate.

Initial studies therefore involved the commercially available monodentate ligand triphenylsilanol, and the bidentate diphenylsilanediol which carry functionalities considered large enough to produce discrete monomeric moieties. It was anticipated that further investigation would centre on a range of siloxide ligands containing two, three or four binding sites.

Thus the silanols, tetramethyl-1,3-dihydroxydisiloxane (S2) and its disodium salt (S1), tetraphenyl-1,3-dihydroxydisiloxane (S5), di-*tert*-butyl-1,1,3,3-tetrahydroxydisiloxane (S7) and heptacyclohexyl-heptasiloxane-1,6,7-triol (S3) were prepared and isolated using literature methods or variations thereof, as indicated in the experimental section of this report. Yields and melting points are in good agreement with those reported in the literature. Selected data are given in table 20.

Cpd	Yield (%)	Mpt (°C)	^{29}Si NMR δ(ppm)[a]	IR data (cm^{-1})[c]	Analysis C	H
S1	96	> 270		3656, 3636, 1258, 986, 945, 851	17.0 (16.0)	7.9 (7.3)
S2	46	59	-10.3	3206, 1262, 1024, 864	28.9 (28.9)	8.6 (8.4)
S3	29	256	-60.5, -68.2, -69.8	3148, 1269, 1129, 1038, 1026, 859	51.8 (51.8)	8.5 (8.2)
S5	48	114	-35.9	3175, 1190, 1127, 1082, 1028, 851	69.2 (69.5)	5.3 (5.2)
S7	59	177-212	-49.5[b]	3120, 1190, 1129, 1009, 895	37.8 (37.8)	9.1 (8.7)

a Recorded in $CDCl_3$ unless otherwise stated; b recorded in CD_3OD; c nujol mull

Table 20 Selected data for silanols

Tetramethyl-1,3-dihydroxydisiloxane disodium salt was prepared through the cleavage of octaphenylcyclotetrasiloxane by addition of a concentrated solution of sodium hydroxide.[8]

$$[Me_2SiO]_4 + 4\,NaOH \xrightarrow[\text{Boil}]{\text{MeOH}} [Me_2Si(ONa)]_2O{\cdot}5H_2O \qquad \textbf{2.1}$$

The salt was isolated as an air stable white powder which displayed sharp, well resolved IR bands at 3636 and 3565 cm^{-1} indicating the presence of co-ordinated water. The disodium salt also exhibited ν(Si-O$^-$Na$^+$) at 945, ν(Si-O-Si) at 986 and δ(Si-CH_3) at 1258 cm^{-1}. Consistently high carbon and hydrogen microanalyses were obtained, even after two recrystallisations, and these are probably due to the incorporation of solvent into the lattice.

Successful conversion of the disodium salt (unrecrystallised material) into the analogous diol (S2) was achieved through careful acid hydrolysis using glacial acetic acid.[8]

$$[Me_2Si(ONa)]_2O.5H_2O + 2\,CH_3COOH \xrightarrow{Et_2O} [Me_2Si(OH)]_2O + CH_3COONa \qquad \textbf{2.2}$$

Strict control of pH, and vigorous stirring of the etheral suspension near the end point of the reaction ensured that yields (table 20) were in accord with those in the literature. The disiloxanediol was isolated as fine white needles which were stored at 0°C to prevent elimination of water and condensation of the product.

A comparison of the IR spectrum of the diol with that of its disodium salt revealed broad Si-OH stretching vibrations at 3206 cm^{-1}, ν(Si-C) at 1262, ν(Si-O-Si) at 1024 and (Si-OH) deformations at 864 cm^{-1}. The ^{1}H, ^{13}C{^{1}H} and ^{29}Si NMR shifts are in good agreement with published values.[196]

Hydrolysis of dichlorodiphenylsilane with water in a dilute etheral suspension of ammonium carbonate eventually produced yields (table 20) of tetraphenyl-1,3-dihydroxydisiloxane (S5) as cited in the literature (51%).[9] Isolation of product (S5) as a major component of the reaction mixture proved to be strongly contingent upon good agitation of the suspension using a mechanical, Hershberg stirrer and slow addition of the dichlorodiphenylsilane.

Attempts to eliminate the use of benzene by extracting the products with toluene/hexane or toluene/petroleum ether (60-80° and 80-100°) mixtures failed. As a result product separation was achieved as described in the literature using mixtures of benzene and petroleum ether (80-100°) in variable proportions.

$$Ph_2SiCl_2 + H_2O \xrightarrow[NH_4CO_3]{Et_2O} Ph_2Si(OH)_2 + [Ph_2Si(OH)]_2O + [HO\{Ph_2SiO\}_3H] + [Ph_2SiO]_n \; n = 3,4 + NH_4Cl \qquad 2.3$$

Main bands in the IR spectrum of disiloxane (S5) may be assigned to ν(Si-OH) at 3175 cm^{-1}, ν(Si-Ph) at 1429 and 1130 cm^{-1}; 1082 and 1028 for ν(Si-O-Si), 887 and 851 for δ(Si-OH), and also 739 and 718 cm^{-1} for $\nu(C\text{-}C)_{phenyl}$.

The ^1H and $^{13}C\{^1H\}$ NMR data show the expected resonances in the aromatic regions of the spectra. A recorded ^{29}Si NMR shift of -35.9 ppm is also in good agreement with published data.[196]

Modifications to the literature preparation of di-*tert*-butyltetrahydroxydisiloxane (S7) were required in order to produce satisfactory yields of product. Following the method of Lickiss[14] *tert*-butyltrichlorosilane was added to a suspension containing ether, water and 3 equivalents of KOH. This gave a slightly acidic solution which was rendered alkaline by the addition of a further equivalent of KOH. However, upon workup after etheral extractions, only extremely low yields of product were obtained (< 2%).

As a result we returned to the original paper by Sommer upon which the method was based.[10] In this *tert*-butyltrichlorosilane was added to 3 equivalents of KOH in a water/ether mixture, the resulting acidic solution was then rendered alkaline by the addition of a further 0.1 mol of KOH. Workup as before realised yields (59%) similar to those documented by Lickiss (69%).

$$tBuSiCl_3 + 3.1\ KOH \xrightarrow{Et_2O,\ MeOH,\ H_2O} [tBuSi(OH)_2]_2O \qquad 2.4$$

Microanalysis, ^1H, $^{13}C\{^1H\}$ and ^{29}Si NMR were in agreement with that expected.[196] The IR spectrum of (S7) consisted of a broad band at 3120 cm^{-1} ν(Si-OH), and absorptions at 1190 and 1129 ν(Si-C), 1009 ν(Si-O-Si), 895 and 866 cm^{-1} as δ(Si-OH).

Slow hydrolytic condensation of cyclohexyltrichlorosilane to yield the trisilanol (S3) occurred following the literature method (see introduction, figure 1).[16] Synthetically useful yields of the analytically pure trisilanol material were obtained from only 25 grams of starting material after a 12 week gestation period with further material continuing to precipitate over the course of 3 years. Separation of the three condensed products was achieved by utilising their differing solubilities in pyridine and diethylether as reported by Feher.[16]

Bands at 1269, 1194 and 1129 cm^{-1} ν(Si-C), 1038, 1026 ν(Si-O-Si), as well as 893, 849 cm^{-1} for δ(Si-OH) were observed in the IR spectrum of the product. ^{1}H, $^{13}C\{^{1}H\}$ and ^{29}Si NMR spectra compared favourably with those documented previously.

Due to their hygroscopic nature, solutions of sodium triphenylsilanolate and disodium-1,1,3,3-tetraphenyldisiloxane diolate were prepared *in situ* (as documented in the literature)[89] by the addition of a THF solution of silanol to a suspension of excess of sodium metal. Unreacted metal was decanted and the solution added *via* cannula to suspensions of the metal precursor.

Sodium triphenylsilanolate was isolated in order to ascertain the effectiveness of this reaction. Recrystallisation from THF/hexane gave large solvated hexagonal crystals which were found to be unsuitable for a structural determination. Examination of the IR spectrum revealed it to be in good agreement with that recorded by Tatlock[197] whilst NMR data confirmed the presence of THF. However due to its hygroscopic nature the analytical data also indicate the incorporation of a single water molecule per $Ph_3SiONa{\cdot}THF$.

IR nujol mull, cm^{-1}	3129 ν(OH_{bound}), 1260 and 1107 ν(Si-Ph), 893 ν(Si-ONa)
Microanalysis. Calc for $C_{22}H_{25}O_3NaSi$	C 68.1 (68.0), H 6.06 (6.50)
^{1}H NMR (d_8-THF)	1.59 (4H, β-CH_2 of THF), 3.45 (4H, α-CH_2 of THF), 6.99 (10H, phenyl meta and para), 7.37 (5H, phenyl ortho)
$^{13}C\{^{1}H\}$ NMR (d_8-THF)	26.1 (β-CH_2 of THF), 67.8 (α-CH_2 of THF), 126.8, 128.7, 130.8, 134.4 (phenyl)

Table 21 Selected analytical data for $Ph_3SiONa{\cdot}THF$ (S8)

2.2.2 TUNGSTEN(OXO)HALIDES

A. INTRODUCTION

High oxidation state chromium, molybdenum and tungsten compounds containing oxo ligands are of great importance in industrial and biological catalysis.[198] In particular oxygen atom transfer reac-

tions involving dioxomolybdenum(VI) complexes are of current interest because of their significance in some biological processes.

$$L_4MoO_2 + X \longrightarrow L_4MoO + OX \qquad 2.5$$

It is assumed that reactions mimicking oxotransferase reactions are also accompanied by the formation of oxo bridged dimers unless ligands of sufficient steric bulk are used to hinder dimer production. Facile oxygen transfer reactions involving molybdenum(VI) centres were thought to occur only when sulfur donor ligands were present in the co-ordination sphere of molybdenum. However this assumption[199]

$$L_4MoO_2 + L_4MoO \longleftrightarrow L_4Mo(=O)-O-(=O)MoL_4 \qquad 2.6$$

has been revised upon discovery of catalytic activity amongst $[Mo_2(O)_2Cl_2L_2]$ compounds (L = DMSO, DMF).[200] A general kinetic treatment of the irreversible forward and reverse oxygen-atom transfer reactions is as shown *vide infra*.[201]

$$MoO_2L_2 + X \underset{}{\overset{k_2}{\rightleftharpoons}} MoOL_2 + XO$$

$$Mo_2O_3L_4 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} MoOL_2 + MoO_2L \qquad 2.7$$

In contrast tungsten does not display oxo-transferase activity.[202] The inactivity of W-containing enzymes may be limited due to its differing redox properties although this has been difficult to substantiate. A second contributory factor is the higher bond order of W=O in comparison with Mo=O, which in compounds such as $[M(O)Cl_4]$ and $[M(O)_2Cl_2]$ has been estimated to amount to a difference of 2.4-4.8 kJ mol^{-1}. The results predict that in oxo transfer a $W^{VI}O_2$ complex would be a poorer oxidant than its Mo(VI) analogue, it also follows that a $W^{IV}O$ complex would be a better reductant than its $Mo^{IV}O$ analogue.

Tungsten displays other notable differences with molybdenum in its chemistry.[203] Relatively few dioxo(VI) compounds have been characterised in comparison to molybdenum, although the limited crystallographic studies indicate that analogous compounds display a close resemblance to one another. The structural motifs are often mononuclear $\{MO_2\}^{2+}$ complexes comprising a distorted octahedral geometry and mutually *cis* oxygen atoms. Examples of binuclear species containing both terminal and bridging oxo groups are known, *e.g.* $K_2[Mo_2O_5(C_2O_4)(H_2O)_2]$ (**139**) exists with both linear and symmetrical Mo-O-Mo bridges. Some oxo tungsten(VI) species also exhibit bridged

structures, *i.e.* $[W_2Cl_6O_4]^{2-}$ and $[W_2O_3(CH_2CMe_3)_6]$ but again few have been structurally characterised.

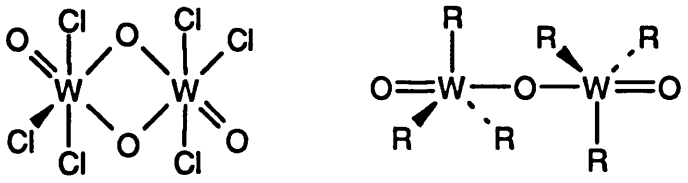


Figure 26 Bridging tungsten(VI) compounds

$[M(O)X_4]$ (M = Mo, W; X = Cl, Br) molecules exist as tetragonal pyramids in the vapour phase but associate *via* oxygen linkages into infinite chains in the crystalline state. As a result the M=O bond lengthens by approximately 0.08 Å.

B. PREPARATION AND CHARACTERISATION

The synthesis of catalytically active molybdenum and tungsten species can be easily achieved *via* oxo- and thio-halide intermediates. A great deal of interest has centred on the oxo- derivatives in view of the of the electronically analogous imido complexes.

Early preparations of oxo-halide species utilised vapour phase reactions in hot tube/furnace procedures, with the products often requiring additional purification. Contemporary approaches reported by Gibson provide a more convenient route which exploit the oxygen (or sulphur) abstraction reactions from bis- silyl (or thio) ethers by metal halides to generate analytically pure materials in high yield.[108] This route was used to generate $[W(O)Cl_4]$ (**M1**) and $[W(O)_2Cl_2]$ (**M2**) by the addition of equimolar amounts of hexamethyldisiloxane in dichloromethane and octane to suspensions of WCl_6 and $[W(O)Cl_4]$ respectively. IR data of both products compared favourably with documented values.

$$WCl_6 + (Me_3Si)_2O \xrightarrow{\text{(i) DCM, 60 min}} W(O)Cl_4 + 2\,Me_3SiCl$$

$$W(O)Cl_4 + (Me_3Si)_2O \xrightarrow[\substack{80\,^{o}C \\ 4\ hrs}]{\text{Octane}} W(O)_2Cl_2 + Me_3SiCl \qquad \textbf{2.8}$$

Tungsten(VI) oxychloride (**M1**) was isolated as an orange powder which could be stored in a Schlenk tube for several weeks under nitrogen. The product hydrolysed rapidly on contact with air to produce white tungsten oxide, WO_3. Tungsten(VI) dichloride dioxide (**M2**) was synthesised as a yellow powder upon heating a suspension of $[W(O)Cl_4]$ with one equivalent of $(Me_3Si)_2O$ in octane to 80°C for 4 hours. Although not as moisture sensitive as $[W(O)Cl_4]$ the product gradually hydrolysed in contact with air and so was stored under nitrogen in a Schlenk tube.

In addition to the parent compounds, $[M(O)_2Cl_2]$ where M = Mo or W, a wide variety of octahedral complexes containing additional donor ligands $[M(O)_2Cl_2(L)_2]$, where L = mono- or bidentate ligand have been characterised and their redox properties investigated. To-date a diverse range of structural studies have been undertaken with ligands including modified sugars,[204] polyethers,[205] ureas,[206] sulfoxides[200] and amines.[207] Complexes may be prepared simply by the direct addition of a ligand to a suspension of the metal dioxo dichloride in a non-co-ordinating solvent, or alternatively by utilising Gibsons procedures in a suitable donor solvent, for example acetonitrile.[108]

Consequently $[W(O)_2Cl_2(L)_2]$ compounds where L = DMSO (M3), TMSO (M4) and $OPPh_3$ (M5), were prepared by addition of excess ligand to freshly prepared acetone solutions of WCl_6.[208a] The compounds crystallised as reasonably air stable white solids in accordance with literature results. Yields, melting points, IR data and microanalysis (table 22) all lie within acceptable ranges of data published.

Compound	Yield %	Mpt (°C)	IR data(cm^{-1})	Microanalysis
$[W(O)Cl_4]$ (M1)	94		ν(W=O) 956	
$[W(O)_2Cl_2]$ (M2)	56		ν(W-O-W) 840, 816	
$[W(O)_2Cl_2(DMSO)_2]$ (M3)	66	80	ν(W=O) 955, 916	C 10.8 (10.8) H 2.87 (2.74)
$[W(O)_2Cl_2(TMSO)_2]$ (M4)	64		ν(W=O) 947, 930	C 19.6 (19.4) H 3.27 (3.26)
$[W(O)_2Cl_2(OPPh_3)_2]$ (M5)	57	278-280	ν(W=O) 959, 913	C 51.0 (51.3) H 3.5 (3.6)

Table 22 Selected data and yields for oxo and dioxo tungsten chlorides

A large number of dioxo- tungsten-, and especially molybdenum-(VI) compounds have been documented.[209] Compounds of the type $[M(O)_2Cl_2]$ M = Mo, W exist as polymers in the solid state, the structure of the tungsten oxo-halide being determined as layers of octahedral WO_4Cl_2 groups which share 4 equatorial oxygen atoms. The oxygen bridges are unsymmetrical, so that in both directions in the layer there are alternate short and long W-O bonds (mean distances 1.67 and 2.28 Å).

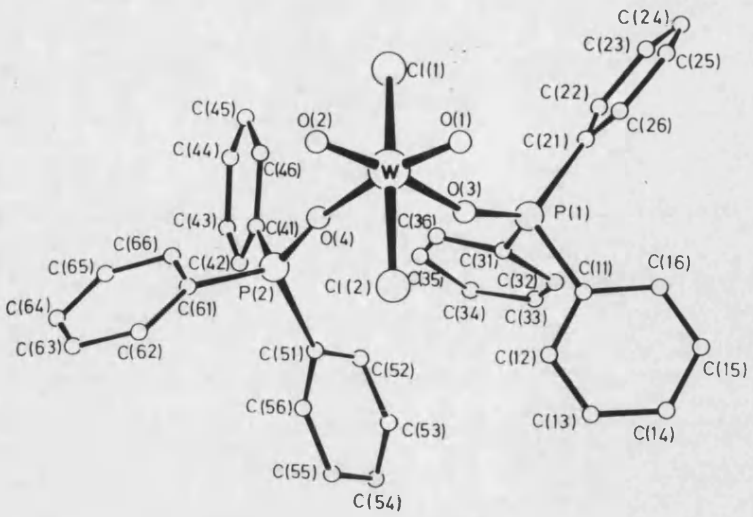


Figure 27 Molecular structure of $[W(O)_2Cl_2(OPPh_3)_2]$

X-ray crystallography of $[M(O)_2Cl_2(L)_2]$ compounds (M = Mo, W) confirm that $\{MO_2\}^{2+}$ is a structurally rigid unit with only small variations in M=O bond length (average 1.704 Å for Mo and 1.709 Å for W complexes) found over a large number of structurally characterised complexes.[210] The *cis*, *trans*, *cis* arrangement of ligands in the distorted octahedral geometry of $[M(O)_2Cl_2(L)_2]$ species is particular favoured as the mutually *cis*-oxo ligands maximise $O(p\pi)\rightarrow M(d\pi)$ bonding. Structurally characterised paradigms include the starting material $[W(O)_2Cl_2(L)_2]$ where L = $OPPh_3$ (Figure 27).[208b]

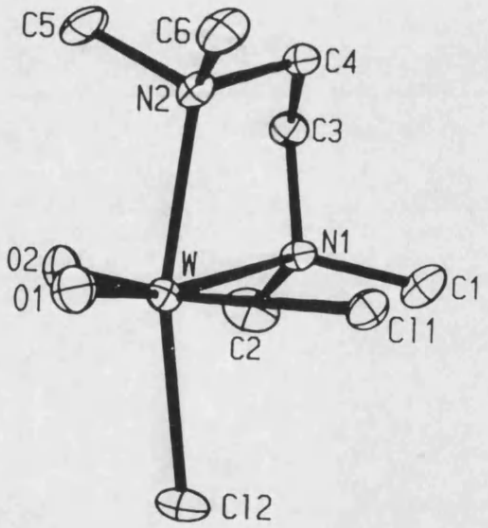


Figure 28 Molecular structure of $[W(O)_2Cl_2(tmen)]$

More recently isostructural molybdenum and tungsten compounds containing a bidentate nitrogen ligand, $[M(O)_2Cl_2(N,N,N',N'$-tetramethylethylenediamine$]$, M = Mo, W have been characterised (figure 28).[207a, b] The geometry approximates to a distorted octahedral arrangement with mutually *cis*-oxo groups but an unusual *cis*-dichloro arrangement. $[W(O)_2Cl_2(tmen)]$, which despite its unusual arrangement still conforms to the rigid $\{MO_2\}^{2+}$ parameters, d(W=O) = 1.705 and 1.711 Å

and an angle O-W-O of 103.3°. The *trans* influence of the oxo ligands is demonstrated by two different W-Cl distances (2.336 Å *trans* to N and 2.440 Å *trans* to O) and two different W-N distances (2.249 Å *trans* to Cl and 2.458 Å *trans* to O).

In determining the reasons for this unusual geometry Dreisch compared the structures of $\{WO_2\}^{2+}$ compounds with the configurations of related imido-complexes, $[M(NR)_2X_2(L)_2]$. The imido group which is isoelectronic with the oxo group adopts many similar structural characteristics, and indicates that the disposition of the ligands is dependent not only upon the steric properties of the ligand but also its electronic interaction with the metal centre.[207b] Thus bulky ligands which possess strong σ-donating properties, *i.e.* PMe_3 or NC^tBu, were found to favour *cis*-oriented chloro ligands.

2.2.3 TUNGSTEN SILOXIDES

A. SALT METATHESIS REACTIONS OF R_3SiONa

Reaction of $[W(O)Cl_4]$ with 3 equivalents of $Ph_3Si(ONa)$ led to the isolation of $[W(O)Cl(OSiPh_3)_3]$ **(P1)**, in 91% yield, as an extremely air and moisture sensitive white powder.

$$W(O)Cl_4 + 3\ Ph_3SiONa \xrightarrow[\text{(ii) Toluene extraction}]{\text{(i) THF, 0 °C 18 hrs}} [W(O)Cl(OSiPh_3)_3] + 3\,NaCl \qquad \textbf{2.9}$$

Prolonged storage in solution during attempts to recrystallise the product, or in efforts to stabilise it with pyridine, led to the formation of a light blue solution from which crystals of triphenylsilanol were recovered. The relatively low stability of oxotungsten(VI) siloxide and alkoxide compounds has been previously noted by Rau[211] and Schrock.[212] The latter noted the rapid decomposition of $[W(O)(=CH^tBu)(O^tBu)_2L]$ where L = PMe_3, PEt_3 and PMe_2Ph, at room temperature.

The hygroscopic nature of the product meant that accurate microanalysis of the product was extremely difficult and is reflected by the inclusion of water in the result obtained. IR data obtained for samples exposed to the atmosphere for even short periods of time also showed the presence of co-ordinated water.

Compound	Expected	Found
$[W(O)Cl(OSiPh_3)_3]$	C 61.1, H 4.28	
$[W(O)Cl(OSiPh_3)_3]\cdot H_2O$	C 60.1, H 4.40	C 60.1, H 4.64

Table 23 Microanalysis for $[W(O)Cl(OSiPh_3)_3]\cdot H_2O$ **(P1)**

Absorptions observed in the IR spectrum are consistent with terminal ν(W=O) at 959 cm^{-1} and ν(W-OSi) at 909 cm^{-1} and in good agreement with analogous oxo tungsten(VI) species (see table

23). Bands due to the triphenylsiloxide groups, ν(Si-Ph), are witnessed at 1428 and 1117 cm^{-1} with $\nu(C\text{-}C)_{ring}$ at 739, 712 and 698 cm^{-1}.

The room temperature ^1H NMR spectrum of (**P1**) exhibits two aromatic resonances with an intensity ratio of 3:2, at 7.2 ppm and 7.7 ppm and are indicative of equivalent phenyl groups. The strong *trans* effect operated by the oxo group would ensure that the weakest π-donor occupies a position opposite. Thus in $[W(O)Cl(OSiPh_3)_3]$ the oxygen and chloride ligands are postulated to occupy the axial sites whilst the siloxide ligands are disposed to the equatorial positions.

Trigonal bipyramidal geometry is documented for 5-coordinate molybdenum, $[Mo(O)_2(OSiPh_3)_2(PPh_3)]$[106a] and tungsten(VI) $[WCl(NSiMe_3)(OSiMe_3)_3]$[213] siloxide compounds. The former exhibits a geometry in which the oxo ligand and the triphenylphosphine group occupy the equatorial positions with the terminal siloxide groups in a mutually *trans* axial arrangement. Equatorial Mo-O(Si) bond lengths are slightly longer [1.922(6) Å] than the axial one [1.903(6) Å] with bond angles of 138.7(4)° and 143.9(4)° respectively.

The Mo atom is not coplanar with the equatorial ligands but is slightly displaced from the equatorial plane toward the axial triphenylsiloxy group. A bond angle between the Mo dioxo bonds of 110.0° indicates that the geometry of the $\{MoO_2\}^{2+}$ unit is apparently unaffected by the uptake of triphenylphosphine. Huang also reported that similar effects were observed with the 2,2'-bipyridine adduct $[Mo(O)_2(OSiPh_3)_2(2,2'\text{-bipyridine})]$.[112a]

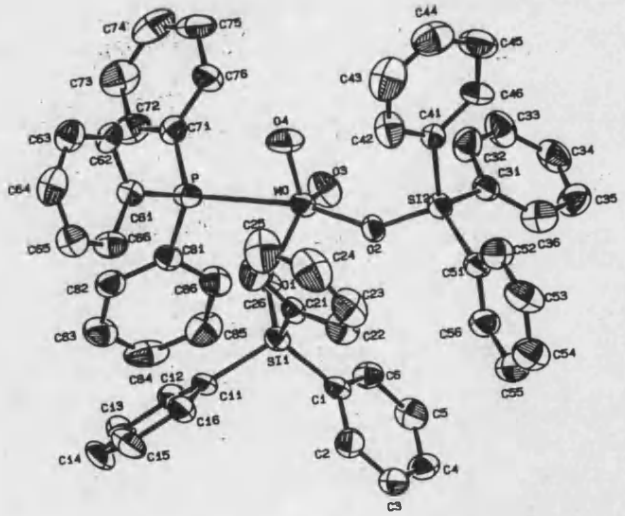


Figure 29 Molecular structure of $[Mo(O)_2(OSiPh_3)_2PPh_3]$

Wilkinson[213] noted the addition of 1,1,1,3,3,3-hexamethyldisilazane to $[M(O)_2Cl_2]$, where M = Cr and Mo, generated $[Cr(O)_2(NSiMe_3)_2]$ and $[Mo(NSiMe_3)_2(OSiMe_3)_2]$. Moreover a tungsten complex, $[W(O)_2Cl_2(dme)]$ reacted with bis(silyl)silazane to form a red oil containing the five co-ordinate complex from which the pyridine adduct $[WCl(NSiMe_3)(OSiMe_3)_3py]$ was isolated.[213] Crystallogra-

phy revealed an octahedral geometry with the W-N(imido) ligand *trans* to the co-ordinating pyridine. The siloxide and chloride groups are disposed to the equatorial positions with W-O(Si) bond lengths in the range of 1.873-1.885 Å.

Curiously, the reactions of $[W(O)Cl_4]$ with Ph_3SiONa appear to be independent of stoichiometric control. Addition of four equivalents of the sodium siloxide to tungsten(VI) oxychloride failed to generate the expected $[WO(OSiPh_3)_4]$ but produced (**P1**) and one unreacted equivalent of sodium triphenylsilanolate. Feher also noted the difficulty in replacing all three (CH_2SiMe_3) groups in the metathesis of $[VO(CH_2SiMe_3)]$ with Ph_3SiOH.[95]

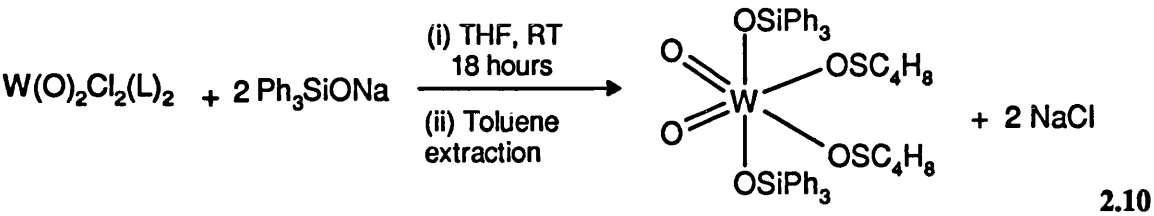
This problem cannot be attributed solely to steric factors as $[WOL_4]$ and $[WOL_4(B)]$ where L = di-acetoneglucose, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose and B = py;[204] L = O^{t}Bu, B = THF[214] and L = $OC_6H_3{}^iPr_2$-2,6[230] have already been prepared and fully characterised. Instead, by considering these examples it would appear that the method of preparation is the limiting factor. This concern was previously highlighted by Clegg[230] in his attempts to generate tungsten(VI) oxotetraalkoxides *via* chloride metathesis with lithium alkoxides. Successful isolation of completely substituted material was only achieved *via* the ammonical metathesis of alkoxides with $[W(O)Cl_4]$ and which resulted in the production of $[\{WO(OR_4\}_2]$ where R = Me, Et, *c*-C_6H_{11} as edge-shared bioctahedra containing asymmetric alkoxide bridges in a coplanar arrangement with the terminal oxo ligands. Cotton also isolated a mononuclear alkoxide by successfully cleaving a binuclear tungsten alkoxide, $[W_2(O^tBu)_6]$ with 4-octyne to yield $[WO(O^tBu)_4(THF)]$.[214] The W-OR bond lengths of both mono- and binuclear products [1.87-1.90 Å] are indicative of some W-OR π-bonding effects.

Attempts to replace the four chloride ligands of $[W(O)Cl_4]$ (**M1**) using a less bulky siloxide, potassium trimethylsilanolate, $KOSiMe_3$, failed. A white air stable powder that was insoluble in all common solvents was isolated from the reaction mixture. IR analysis of the solid showed the presence of ν(W-O-W) at 900-700 cm^{-1}, ν(Si-Me) 1154, 1252 cm^{-1} similar to those observed by Gibson, who noted the formation of a heavily oxo-bridged tungsten siloxide upon prolonged exposure of $[W(O)Cl_4]$ to Me_3SiCl.[108] Analogous reactions using $[W(O)_2Cl_2(DMSO)_2]$ (**M3**) also gave an insoluble, air stable white powder which the IR spectrum (broad ν(W-O-W) at 950-780 and ν(Si-Me) 1156 cm^{-1}) indicated to be another bridged oxo-tungsten siloxide.

IR and X-ray powder investigations of $[WO(OR)_4]$ (R = Me, Et), prepared by metathesis reactions of $[W(O)Cl_4]$ with NaOR have showed them to be oxo-bridged polymeric species, analogues of $[W(O)Cl_4]$.[215] These structures are very different to those of the binuclear molybdenum oxo-alkoxides analogues prepared by metathesis reactions using alcohols. Structural differences are understood to arise from the presence of traces of bonded NaOR and which is irremovable by

recrystallisation. It is however interesting to note that polymerisation of $[Mo(OR)_4]$ where R = Et, ^{i}Pr but not Me, may also be achieved in the presence of NaOR but only by the formation of alkoxo-bridges. *A priori* it is believed that the differences in chemical and structural characteristics lie in the higher multiplicity and lower donor ability of Mo=O in comparison with W=O.

Investigations into the product (**P2**) obtained from the reaction of $[W(O)_2Cl_2(TMSO)_2]$ with Ph_3SiONa were in good accord with the electronically favoured distorted octahedral geometry observed for a *cis, trans, cis* disposition of ligands.



2.10

Compound (**P2**) was isolated as a reasonably air and moisture sensitive powder in 77% yield from the reaction of two equivalents of sodium triphenylsilanolate to one of the metal centre (**M4**). Decomposition of the compound in solution over a period of only two days hindered attempts to grow suitable crystals for a structural determination, but repeated efforts at purification of the compound produced microanalysis which were within acceptable limits.

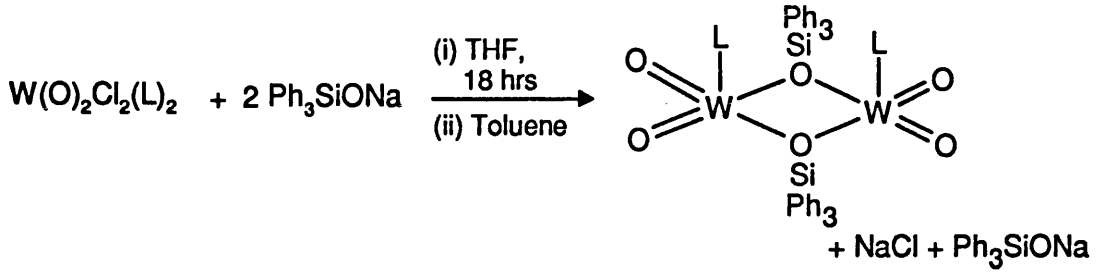
Interpretation of the infrared spectrum is hindered by the difficulty in confidently assigning individual bands at 893, 931, 945 and 1001 cm^{-1} to W-O, S-O or W-O(Si) vibrations. Patterns are nonetheless concordant with an octahedral monomer containing no bridging oxo ligands with the two intense peaks at 945 and 931 cm^{-1} characteristic of the symmetric and asymmetric metal-oxo stretching vibrations of a *cis*-dioxo configuration.[216] The third intense band located at 893 cm^{-1} is consistent with other W-O(Si) stretching vibrations we have observed in tungsten siloxides (see table 23).

The ^{1}H NMR spectrum showed unresolved multiplets at 0.9, 1.9, 2.3 and 2.7 ppm indicative of the equivalent TMSO ligands, as well the expected resonances at 7.15 and 7.8 ppm in the aromatic region of the spectrum. Thus the strongly σ-donating, but poorest π-donor ligand, TMSO, should occupy the equatorial positions *trans* to the oxo groups with the stronger π-donating siloxides residing in the axial sites.

Attempts at preparing the dimethylsulfoxide and triphenylphosphine oxide analogues were hindered by their high sensitivity to moisture. Initial efforts to react the tungsten dichloride dioxide compounds (**M3**) and (**M5**) with pre-prepared sodium triphenylsilanolate produced complex mixtures of products and often led to the isolation of triphenylsilanol. A single product was only isolated when

freshly prepared solutions of Ph_3SiONa were used, which probably reflects the extreme susceptibility of the products to hydrolysis.

Eventually reaction of two equivalents of Ph_3SiONa with one equivalent of $[W(O)_2Cl_2(L)_2]$ where L = DMSO, $OPPh_3$ led to the isolation of white powders $[W(O)_2(\mu\text{-}OSiPh_3)L]$ L = DMSO (P3), and L = Ph_3PO (P4) which defied all attempts to produce crystals. IR, microanalysis, ^1H, and $^{13}C\{^1H\}$ NMR spectra are tentatively interpreted in terms of two 5-co-ordinate tungsten centres, containing mutually *cis*-oxo ligands and an axial neutral donor, and linked by 2 bridging siloxides.



2.11

Compound	Calculated for	Expected	Found
P3	$C_{40}H_{42}O_8S_2Si_2W_2$	C 42.2, H 3.72	C 42.4, H 3.85
P4	$C_{72}H_{60}O_8P_2Si_2W_2$	C 65.3, H 4.58	C 68.8, H 5.16

Table 24 Microanalysis for $[W(O)_2(\mu\text{-}OSiPh_3)L]_2$ compounds

Extraction of (P3) with toluene and removal of the solvent gave the product as an analytically pure material, however (P4) could not be purified completely.

IR absorptions representative of a *cis* metal-oxo grouping occur at 945 and 920 cm^{-1} for $[W(O)_2(\mu\text{-}OSiPh_3)(DMSO)]_2$ (P3), 964 and 911 cm^{-1} for $[W(O)_2(\mu\text{-}OSiPh_3)(OPPh_3)]_2$ (P4). The intense W-O(Si) stretching frequency at 893 cm^{-1} observed for the mononuclear TMSO adduct is shifted to 889 cm^{-1} for both the DMSO and $OPPh_3$ adducts.

The ^1H NMR spectrum of (P3) shows two multiplets in a ratio of 3:2 at 7.16 and 7.73 ppm, accordant with equivalent phenyl groupings and a singlet at 1.53 ppm ascribed to the dimethylsulfoxide ligands. Compound (P4) also shows only a single environment for the triphenylsiloxide (7.1 and 7.9 ppm) and triphenylphosphine oxide (6.9 and 7.5 ppm) ligands. The simple pattern of the spectra indicates the symmetrical nature of the products and is consolidated by the $^{13}C\{^1H\}$ spectra which display chemical shifts in accord wit

h isolated compounds containing bridging triphenylsiloxide groups.[79]

Isolation of these bridging siloxide species (P3) and (P4) was particularly suprising given that $[M(O)_2(OSiR_3)_2]$ (where M= Cr, Mo and R = ^{t}Bu) are reasonably stable compounds that have been

characterised.[106a, 217] Of particular note is that once again the successful synthesis of these compounds was achieved *via* silylation of an M=O function or by metathesis with triphenylsilanol and **not** by reaction of an alkali metal salt.

However, the disposition to form monodenate or bridging binding modes is not solely determined by the preparative route used. For example metathesis reactions leading to the generation of homoleptic alkoxide compounds containing M-M bonds often display either terminal or bridging modes and under certain circumstances a combination of both. The latter configuration is more prevalent amongst the less bulky alkoxides with the facile interchange of binding arrangements allowing for the optimisation of metal-metal and metal-ligand interactions. Structurally characterised examples are exemplified by Chisholms' syntheses of $[W_4(O)(O^iPr)_{10}]$ and $[W_4(O)(Cl)(O^iPr)_9]$.[218]

In contrast there is little variation of binding mode in transition metal siloxide moieties. The chemistry of the monodentate ligands is dominated by their predilection to form terminal bonds with a metal centre. Only a few well characterised examples of bridging siloxides exist, *e.g.* M = Rh, R_3SiO where R = Ph, Me,[79] M= Al, R = Me, Et, Ph. Addition of excess pyridine to $[CrO_2(NSiMe_3)_2]$ also results in a five-co-ordinate chromium(V) dimer, $[CrO(NSiMe_3)(\mu\text{-}OSiMe_3)(py)]_2$, containing bridging trimethylsiloxide moieties which were isolated and characterised by Wilkinson.[213]

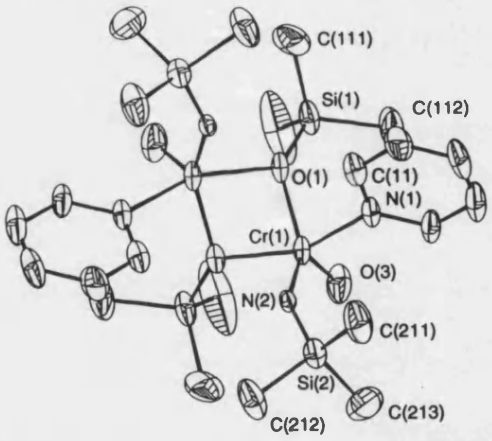
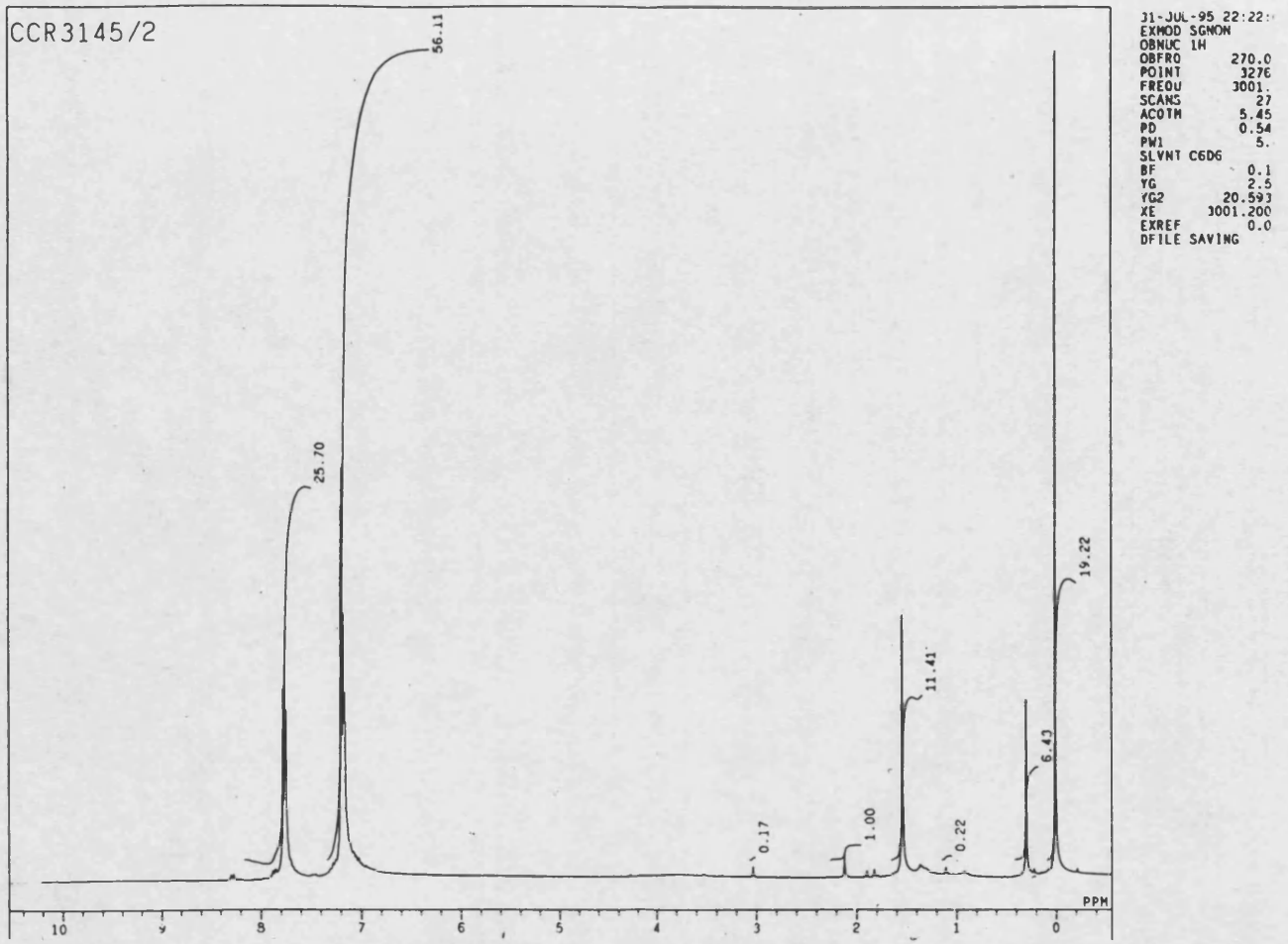


Figure 30 Molecular structure of $[CrO(NSiMe_3)(\mu\text{-}OSiMe_3)(py)]_2$ (**140**)

The geometry at the chromium centres lies midway between trigonal bipyramidal and square pyramidal and contains slightly asymmetric bridging siloxide groups (figure 30). *Tert*-butylimido complexes of rhenium formed by the reaction of $[ReO_3(OSiMe_3)]$ with $[^tBuNH(SiMe_3)]$ have also been found to exhibit both bridging and terminal trimethylsiloxide ligands.[219]



Integrated intensities not to scale

Figure 31 The ^{1}H NMR spectrum of $[W(O)_2(\mu\text{-}OSiPh_3)DMSO]_2$

Studies of oxo-transferase reactions in dioxo molybdenum(VI) systems,[199] in particular those involving oxo/sulfido ligand substitution of $[Mo_2O_7]_2^-$, have led to the isolation of moieties containing bridging siloxide ligands. Structural characterisation of the $[MoS_3(OSiMe_3)]^-$ anion **(141)** confirms the presence of bridging trimethylsiloxide moieties.[118]

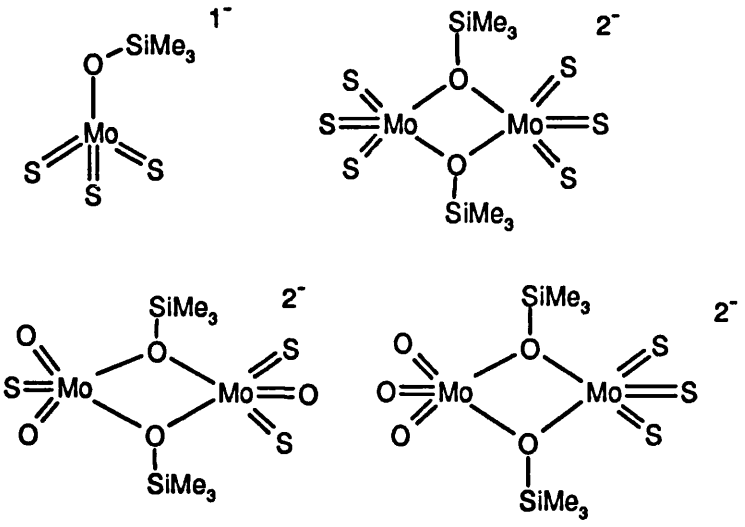


Figure 32 Possible intermediates relevant to oxo-transferase reactions

Compound	ν(W=O) cm^{-1}	ν(W-O-Si) cm^{-1}
$[W(O)_2Cl(OSiMe_3)]$	700-900	1002
$[W(O)_2Cp^*\{OSi(PhCH_2)_3\}]$	947, 877	779
$[W(O)_2Cp^*(OSi^tBu_2H)]$	918, 895	822
$[W(O)_2Cp^*(OSiMe_2{}^tBu)]$	913, 890	834
$[W(O)_2Cp^*(OSiMe_3)]$	897, 891	846
$[WCl(NSiMe_3)(OSiMe_3)_3(py)]$		913
$[W(N^tBu)_2(\mu\text{-}OSi^tBu_2O)]_2$		981
$[W_2(OSiPh_3)_2(NMe_2)_4]$		910
$[W_2(OSiPh_3)_4(NMe_2)_2]$		920
[WOcalix[4]arene(CH_3COOH)]	961	

Table 25 Infra-red data for tungsten oxo and dioxo siloxide and related compounds

B. Reactions of $[R_2SiO]_n$ compounds

(i) Ring opening reactions of $[R_2SiO]_n$ where n = 3 or 4

Tungsten hexachloride reacts with hexaphenylcyclotrisiloxane in dichloromethane or acetonitrile to generate moderate to high yields of tungsten oxychloride (M1). Its IR spectrum was is in good agreement with published data.[108]

$$WCl_6 + [Ph_2SiO]_3 \xrightarrow[\text{(ii) MeCN, 3 days}]{\text{(i) DCM, 60 min}} W(O)Cl_4 \qquad \textbf{2.12}$$

Isolated yields (64% DCM, 82% MeCN) are lower than those obtained (99%) from the reaction of tungsten hexachloride with hexamethyldisiloxane. It is interesting to note that neither $[WCl_4(NCMe)_2]$ (equation 2.13) nor $[W(O)Cl_4]$ with co-ordinated acetonitrile (equation 2.12ii), was obtained after washing with toluene and exposure to mild vacuum. This indicates the highly oxo-philic nature of the tungsten centre and the weakly co-ordinating nature of the acetonitrile ligand *trans* to a W=O bond.

$$WCl_6 + MeCN \xrightarrow{\text{Room temp}} WCl_4(NCMe)_2 \qquad \textbf{2.13}$$

Prolonged reaction of WCl_6 with hexaphenylcyclotrisiloxane in THF generated a dark blue viscid oil containing mixed oxidation state tungsten moieties. The colour changes observed (brown to green and finally blue) are similar to those noted in the formation of $[W(O)Cl_3(THF)_2]$ **(143)** from WCl_6 and THF,[203] but no tungsten containing material could be isolated.

$$WCl_6 + THF \xrightarrow{\text{Room temp}} W(O)Cl_3(THF)_2 \qquad \textbf{2.14}$$

Thus the blue liquor was oxidised using 30 vol. hydrogen peroxide to give an insoluble tungsten oxide and a colourless solution which when stored at low temperature for 7 days produced a sticky white solid.

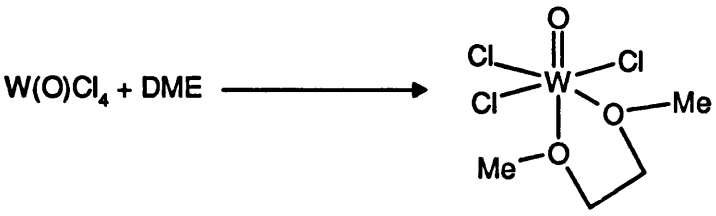
Decanting the solvent gave a solid that melted rapidly upon reaching room temperature, and which analysis indicated to be an unknown molecular weight ring-opened THF polymer **(P5)**.[220]

Microanalysis (calc for C_4H_8O)	Found C 66.6 (66.7); H 11.20 (11.20)
IR data (cm^{-1})	1113 ν_{asym}(C-O)
NMR data ($CDCl_3$)	^{1}H NMR: 1.63 $OCH_2CH_2CH_2CH_2O$, 3.47 $OCH_2CH_2CH_2CH_2O$ ^{13}C NMR: 26.5 $OCH_2CH_2CH_2CH_2O$, 34.1 $OCH_2CH_2CH_2CH_2O$

Table 26 Selected analytical data for THF polymer **(P5)**

Catalysis of metathesis reactions and ring opening polymerisations by a wide variety of tungsten based species have been noted previously. Although the active component(s) of most systems remain poorly defined the reactive moiety is generally potent, *i.e.* addition of allytrimethylsilane to WCl_6 in etheral solvents catalyses both the metathesis of olefins and the ring opening polymerisations of cyclic olefins.[221] In the latter example, attempts to elucidate the active catalyst resulted in the isolation of $[WCl_5(OEt_2)]$ **(142)** as the major product. The propensity for oxygen abstraction and co-

ordination reactions in high oxidation state early transition metal chemistry has been well documented. For example $[W(O)Cl_3(THF)_2]$ **(143)** has been isolated upon dissolution of WCl_6,[203] or $[WCl_5(OEt_2)]$ **(142)** in THF, whilst the compound $[W(O)Cl_3(DME)]$ **(144)** has also been characterised (see reaction 2.15).[221]

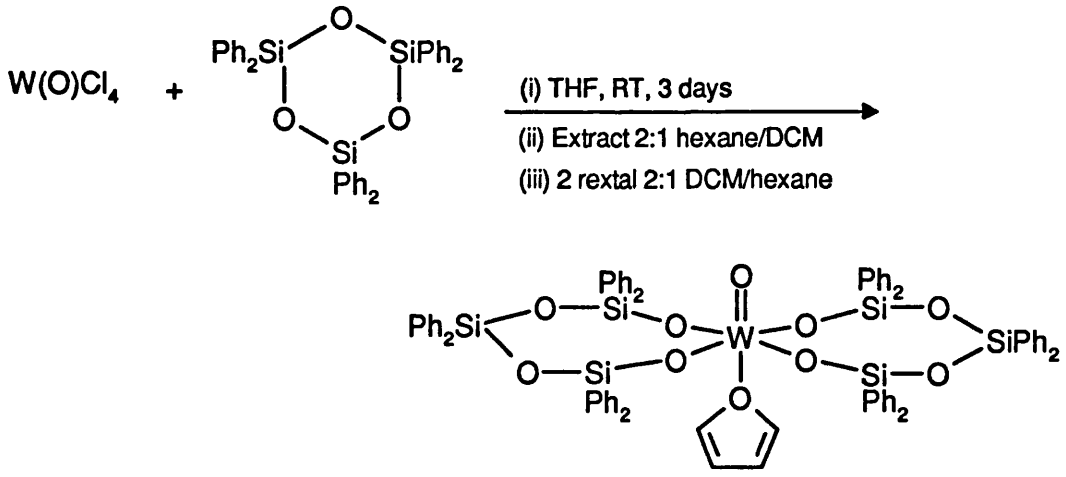


2.15

However earlier precedents suggest that siloxane reagents are the preferred source of oxygen in such reactions and therefore in the absence of such products it is likely that the formation of a tungstasiloxane intermediate is responsible for the ring opening polymerisation of THF.

Reaction of WCl_6 with octaphenylcyclotetrasiloxane also produced a viscid blue oil but no tungsten(VI) oxychloride, tungsten siloxide or THF species could be isolated. This ring system also failed to yield isolable material when reacted with $[W(O)Cl_4]$, but an air stable spirocyclic tungsten siloxide was found in low yield (9%) upon reaction of **(M1)** with hexaphenylcyclotrisiloxane for 3 days. Isolation of $[WO\{O(OSiPh_2)_3\}_2 \cdot THF]$ **(P6)** represents an unprecedented report of a tungsten siloxane species formed by the insertion of a metal centre into a cyclosiloxane.

Small needles of **(P6)**, suitable for single crystal analysis were isolated after a second recrystallisation of the crude product, $[WO\{O(OSiPh_2)_3\}_2 \cdot 2THF]$ **(P7)** from a 2:1 dichloromethane-hexane mixture.



2.16

Compounds **(P6)** and **(P7)** display a strong, sharp band in their IR spectra at 968 cm^{-1} which is indicative of ν(W=O) in an unbridged mode, and contrasts well with that of the broad band at 880-

900 cm^{-1} seen in the oxo bridged $[W(O)Cl_4]$ structure. Strong, sharp absorptions at 914 cm^{-1} ν(W-OSi), 1028 and 1076 cm^{-1} ν(Si-O-Si) are indicative of a relatively unstrained heterosiloxane.

^1H and $^{13}C\{^1H\}$ NMR spectra of the crude product (**P7**) show the presence of two, chemically distinct molecules of THF. A singlet and a quartet at 1.18 and 3.34 ppm respectively in the ^1H NMR spectrum and singlets at 23.9 and 68.1 ppm in the carbon spectrum are attributed to the THF co-ordinated to the tungsten centre. Resonances at 1.54 (quartet) and 3.42 (triplet) ppm in the proton spectrum and at 25.5 and 69.6 ppm in the $^{13}C\{^1H\}$ NMR spectrum are ascribed to solvent within the lattice which a second recrystallisation of the product removed.

Metal-halide metathesis reactions have been used to synthesise oxo- and dioxo-transition metal cyclosiloxanes, including a six-membered oxovanadium(IV) cyclosiloxane and a number of similar spirocyclic transition metal siloxanes, $[M\{O(Ph_2SiO)_3(L)_2]$ M = Ti, Hf, L = py; M = Sn, L = THF.[74] ^{29}Si NMR spectroscopy exhibits two distinct silicon environments in these eight-membered metallasiloxane ring compounds. Shifts for the tungsten [δ -40.5 (SiOSi) and -44.1 (SiOW) ppm] and titanium [δ -41.8 (SiOSi) and -43.7 (SiOTi) ppm] compounds reveal a slightly more shielded environment than those in the tin compound [δ -34.7 (SiOSi) and -40.6 (SiOSn) ppm]. The five resonances observed in the hafnium analogue [-26.8, -45.7, -49.4, -50.0, -51.2 ppm] have been rationalised on the existence in solution of both *cis* and *trans* isomers (three resonances for *cis* and two for *trans*).

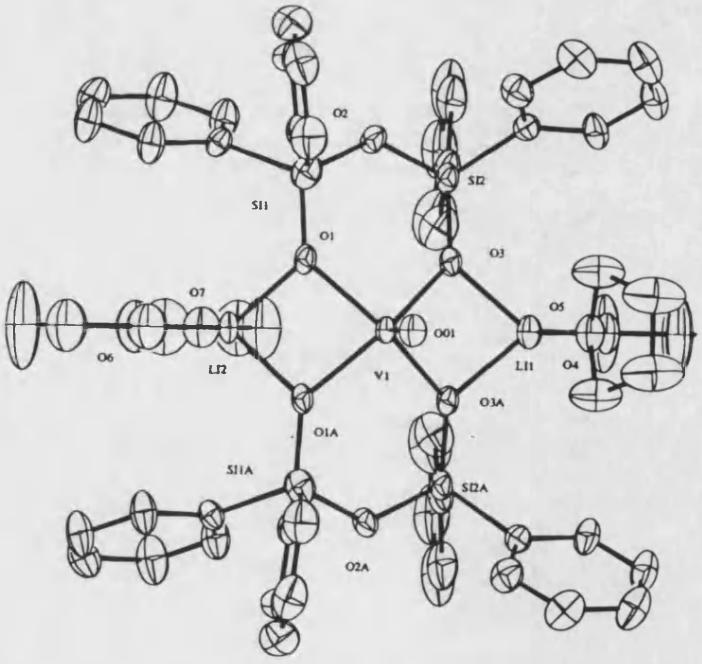


Figure 33 Molecular structure of $[VO\{O\{SiPh_2O)_2\}_2$-μ-$(Li(THF)_2)_2]$

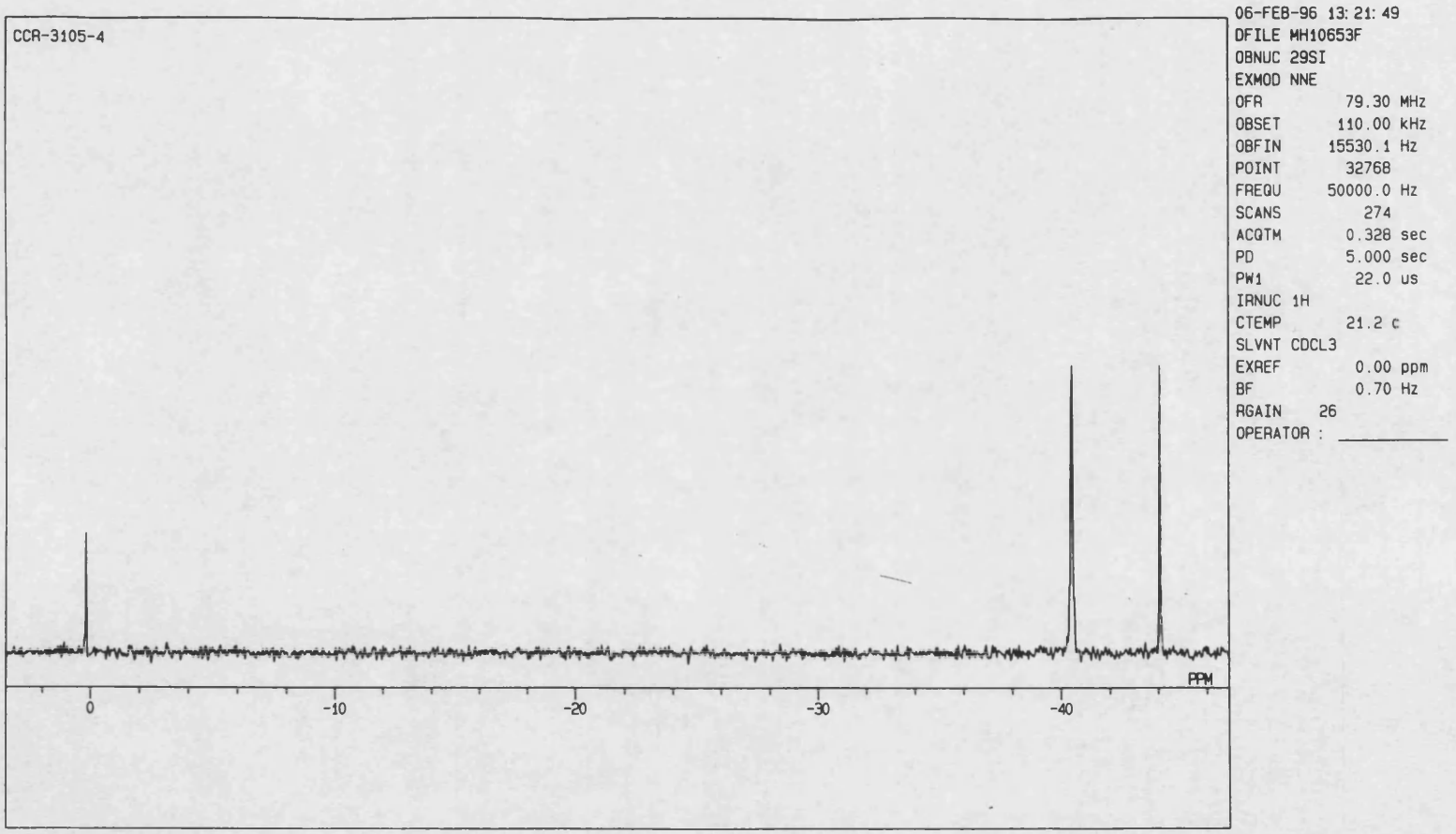


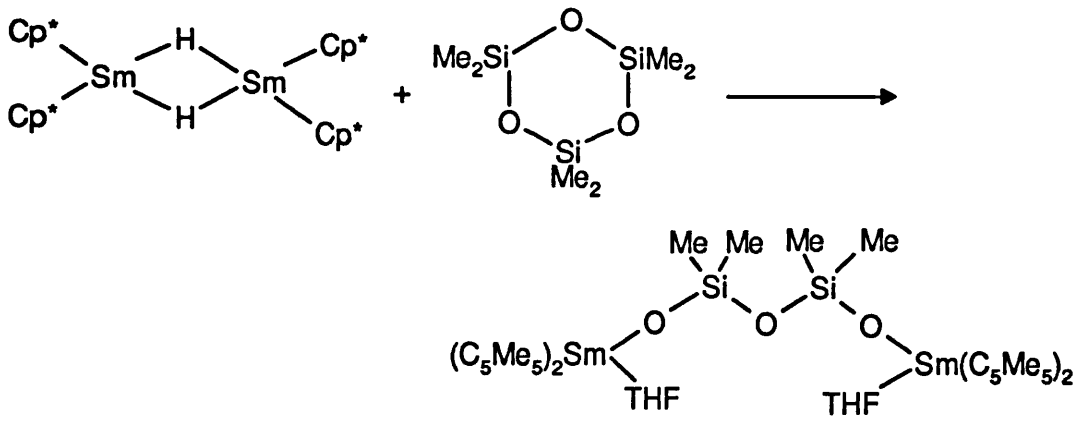
Figure 34 The ^{29}Si NMR spectrum of $[WO\{O(Ph_2SiO)_3\}_2 \cdot THF]$ (**P6**)

(ii) Mechanistic Aspects of Ring Opening Reactions

The formation of **(P6)** illustrates the known difference in reactivity of the planar cyclotrisiloxanes and the less strained, puckered cyclotetrasiloxanes. For example the base catalysed (KOH, $KOSiMe_3$) ring-expansion of $[Ph_2SiO]_4$ is 95% complete after 18 hours at 140°C, whereas polymerisation of $[Ph_2SiO]_3$ occurs 50 times faster (*i.e.* complete within 21 minutes). The increased strain within the cyclotrisiloxane ring system is apparent from crystallographic studies which show reduced $SiOSi_{av}$ bond angles for $[Ph_2SiO]_3$ (132-133°) in comparison to $[Ph_2SiO]_4$ (152-167°).[222]

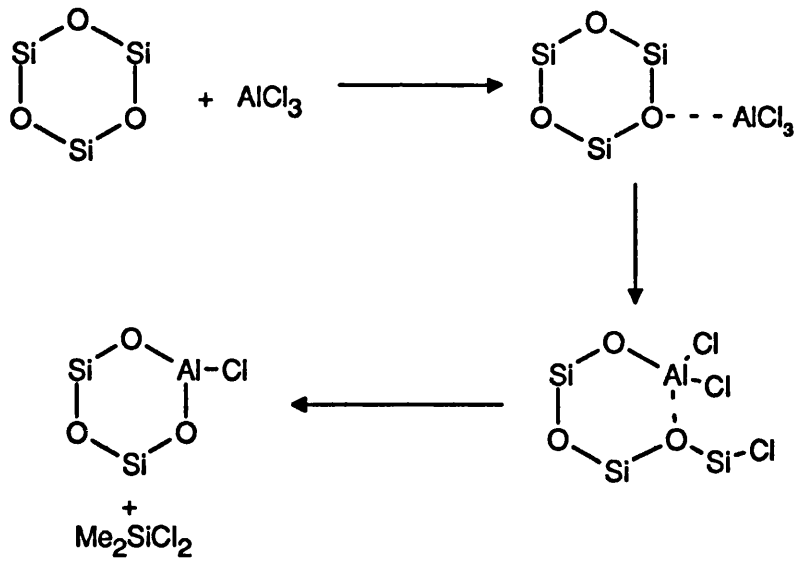
Ring-expansion processes may occur in an analogous manner to base-catalysed ring opening polymerisations. Thus nucleophilic attack at a silicon centre has been envisaged in the conversion of poly(dimethylsiloxane) to the thallium ladder polymer complex $[\{Tl_2(OSiMe_2)_2O\}_2]_n$ and the formation of $[Sm(C_5Me_5)(THF)_2]_2(\mu\text{-}OSiMe_2OSiMe_2O)]_2$ **(145)** occurs similarly.[112]

Evans *et al.* isolated **(145)** by reaction of the highly reactive, oxophilic $[Sm(C_5Me_5)_2(\mu\text{-}H)]_2$ with silicone grease. Commercial silicone grease is reported to consist primarily of polydimethylsiloxane (>80%), dimethylcyclosiloxane (<1%, unknown ring size) and hydroxy terminated dimethylsiloxane (5-10%).[223] Reactions were observed with individual components of the silicon grease, *e.g.* decamethylcyclopentasiloxane, decamethyltetrasiloxane, and octamethylcyclotetrasiloxane in both alkane and THF solvents, but none produced **(145)**. However, the reaction of $[Sm(C_5Me_5)_2(\mu\text{-}H)]_2$ with hexamethylcyclotrisiloxane in THF generated the samarium siloxide which was then fully characterised.



2.17

Titanium tetrachloride is reported to undergo ring opening reactions of cyclic siloxanes to produce linear, long chain heterosiloxane polymers, whilst aluminium trichloride generates cyclic heterosiloxanes.[12] Reaction of $AlCl_3$ with $[Me_2SiO]_3$ produces a six-membered ring containing a single Al atom whilst an eight-membered ring is isolated upon reaction with octamethylcyclotetrasiloxane.



Methyl groups omitted for clarity
Figure 35 Mechanism for reaction of $AlCl_3$ with $[Ph_2SiO]_3$

The driving forces for the insertion of a tungsten centre in a six-membered ring are (a) the expected higher electrophilicity of silicon in a six-membered ring compared to an eight-membered ring, and (b) the relief of ring strain on opening the cyclotrisiloxane ring system.

Polar aprotic solvents such as THF are known to promote reactions involving charged intermediates, such as Grignard reagents, living polymerisations and those proceeding *via* nucleophilic substitution.[224] Ionic reactions are catalysed by the stabilisation of the cationic intermediates by linkage to the oxygen lone pairs of electrons resident on the etheral solvent.

The role of THF in sustaining the reactions was investigated by repeating the procedure in various media. Stabilisation of the oxophilic $[W(O)Cl_4]$ centre has been reported to occur through adduct formation with a variety of oxygenated solvents (see reaction 2.18).

$$W(O)Cl_4 + L \xrightarrow{L = THF,\ Et_2O,\ (CH_3)_2CO} W(O)Cl_4(L) \qquad \textbf{2.18}$$

Thus, unsurprisingly replicating the reaction in dichloromethane led to the formation of an intractable blue oil from which only tungsten oxide and the unchanged cyclosiloxane could be recovered. On replacing THF with another polar, co-ordinating solvent, acetonitrile, no tungsten siloxane species were isolated. The greater co-ordinating ability of acetonitrile may stabilise the polar intermediates to such an extent that the reaction no longer proceeds.

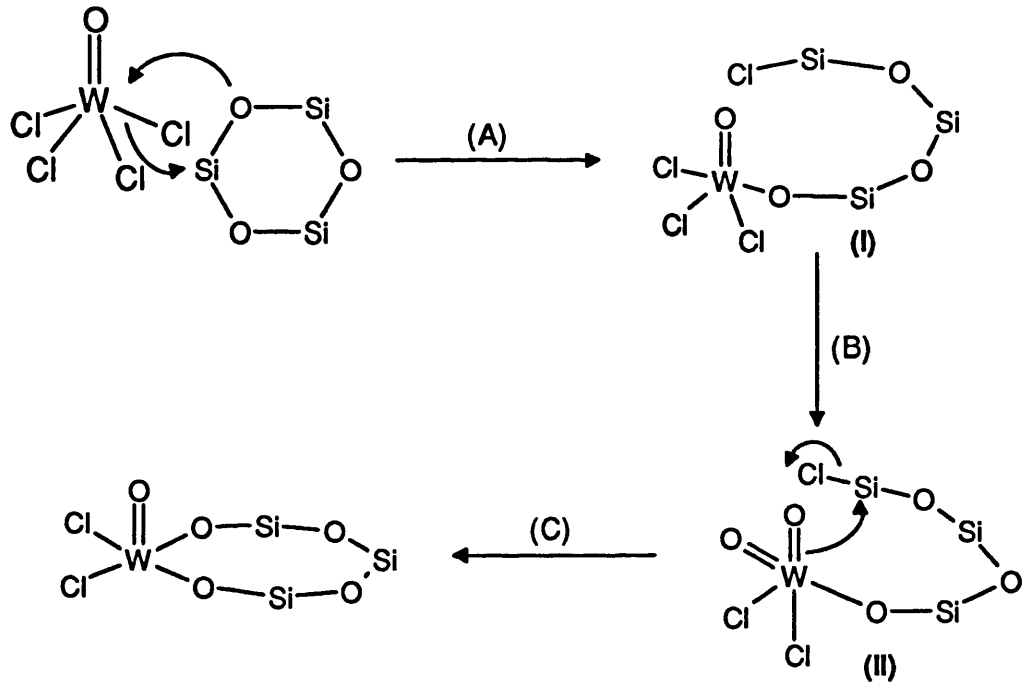
The use of cyclosiloxanes also confers an additional avantage over bis(silyl)ethers in substituting the chloride ligands of (M1), in which Gibson noted that it was not possible to replace all the chloride

groups on tungsten oxychloride with oxo ligands.[108] Addition of 2 equivalents of $(Me_3Si)_2O$ to $[W(O)Cl_4]$ generating only $[W(O)_2Cl(OSiMe_3)]$ as a stable, pale blue, microcrystalline solid.

$$W(O)Cl_4 + 2(Me_3Si)_2O \xrightarrow{DCM,\ 60\ min} W(O)_2Cl(OSiMe)_3 + 2\,Me_3SiCl \qquad \textbf{2.19}$$

In contrast, $[W(O)Cl_4]$, already noted as a ring opening polymerisation catalyst,[225] replaced all four chloride ligands in yielding $[WO\{O(OSiPh_2)_3\}_2 \cdot THF]$ (P6). The driving force for complete susbstution may be (a) the favourable thermodynamic factors caused by the ring opening of hexaphenylcyclotrisiloxane, (b) the highly oxophilic nature of the tungsten centre and (c) the prior co-ordination of a siloxane chain terminated with a reactive end group (see figure 36).

Synthesis of (P6) may occur through the initial ring opening step (A) shown in figure 36. It is postulated as a nucleophilic attack by an oxygen atom from the siloxane ring at the tungsten centre to form the initial W-O(Si) linkage and terminate the siloxane chain with a reactive Si-Cl bond. The formation of (I) is analogous to that of $[W(O)Cl_3(OSiMe_3)]_x$ formed as an intermediate in the oxygen transfer reaction of $[W(O)Cl_4]$ to $[W(O)_2Cl_2(tmen)]$.[207]



Phenyl groups omitted for clarity

Figure 36 Possible mechanism for the formation of $[WO\{O(SiPh_2O)_3\}_2 \cdot THF]$

Step (B) involves the formation of a second tungsten-oxygen bond. Positioning of the second oxo ligand in a mutually *cis*- disposition ensures that the $O(p\pi) \rightarrow W(d\pi)$ interactions are maximised.

Abstraction of a second oxygen atom from a cyclosiloxane ring or alternatively from THF[221] thus generates (II).

The attack of metal-oxo bonds by reactive Si-Cl functionalities are well documented methods for the formation of transition metal siloxides.[226] Hence, the last step (C), involves the ring closure of the siloxane ring through attack of the oxo ligand at the terminal silicon centre. Thus an eight membered ring is formed with the chelating oxygen atoms in a mutually *cis* orientation. This process may then be repeated on the second pair of chloride ligands to produce the second eight-membered ring. Compound (**P6**) is probably generated as a minor product because of the competing, apparently facile silicon-oxygen heterolysis, consistent with the well documented oxophilicity of tungsten oxychlorides.[227]

In light of the greater reactivity demonstrated by the strained cyclosiloxane, it is suprising that $[W(O)_2Cl_2(DMSO)_2]$ failed to react with $[Ph_2SiO]_3$ in a similar manner. Even under more forcing conditions, reflux for 3 hours, no evidence of ring opening was observed and both reactants were isolated unchanged. This may reflect the increased steric saturation of the metal centre, which, is also rendered less oxophilic by co-ordination to the good σ- donating DMSO ligands.

(ii) Condensation of Bidentate Silanolate Precursors in Salt Metathesis Reactions

Ring expanded products are also formed for certain combinations of metal chloride and disiloxanediolate reagent over a wide range of reaction conditions (see introduction, figure 19). In these examples there appears to be no correlation between the formation of ring expanded products and the nature of the cation in the reagent $[(Ph_2SiO)_2O]^{2-}$ (M = Li, Na), the size of the target metal centre or the stoichiometry of reagents employed.[74]

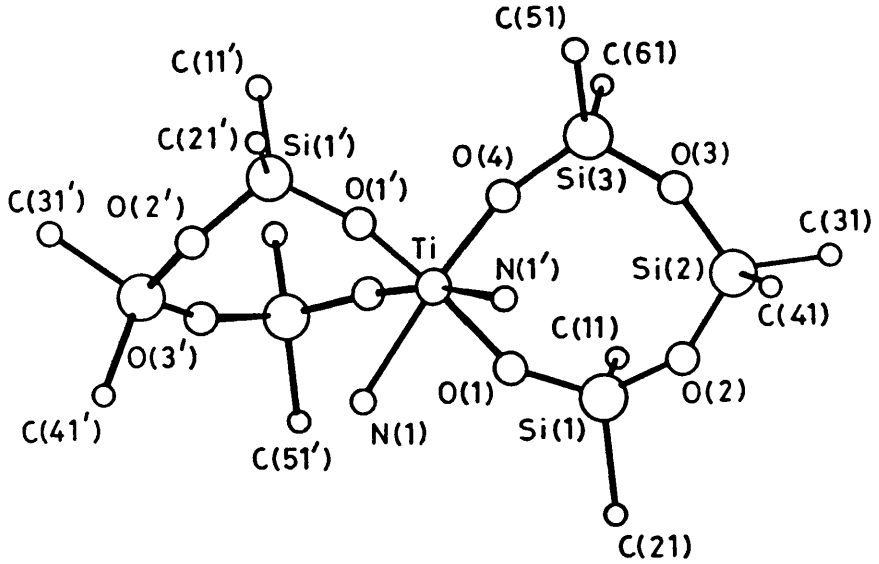


Figure 37 Molecular structure of *cis*-$[Ti\{O(Ph_2SiO)_3\}_2(py)_2]$

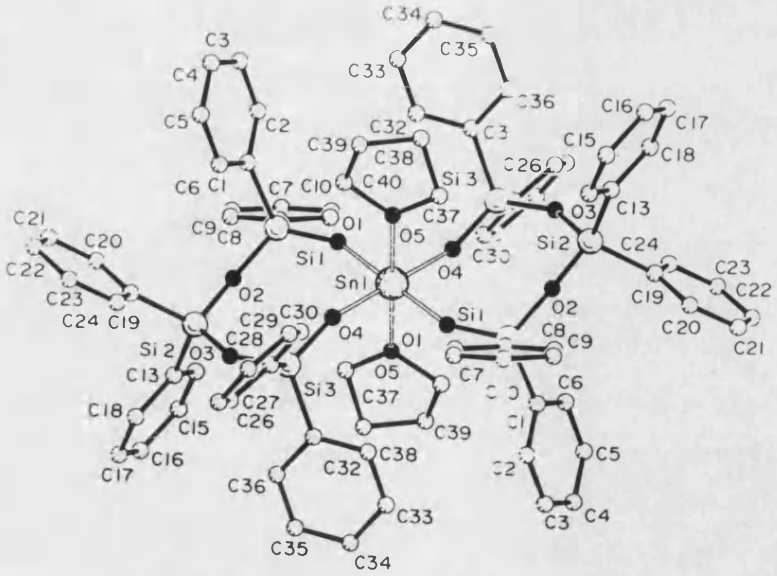
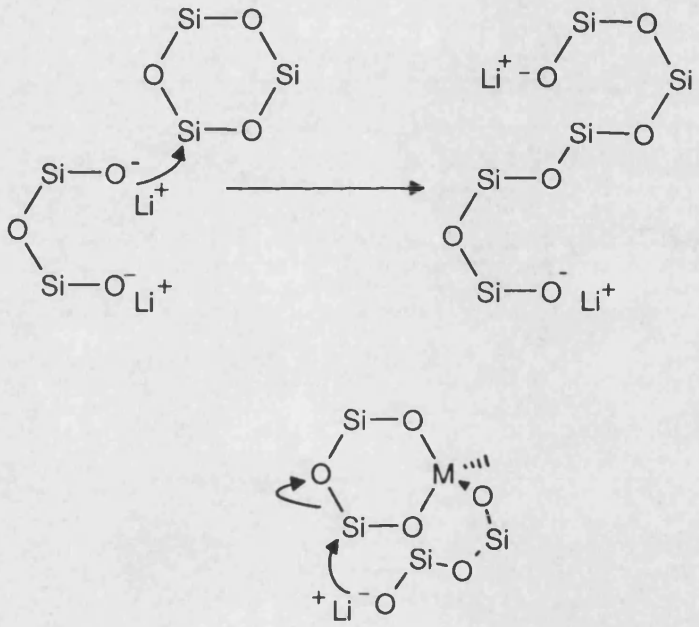


Figure 38 Molecular structure of $[Sn\{O(Ph_2SiO)_3\}_2(THF)_2]$

Mechanistically expansion could proceed *via* (a) attack at silicon in a six-membered metallasiloxane ring by free siloxanediolate or (b) attack by disiloxanediolate co-ordinated at one end of a metal centre. Sullivan found the reaction rates of lithium silanolate precursors were too fast to ascertain intermediate species by ^{29}Si NMR studies, and that rapid exchange of lithium environments rules out ^{7}Li NMR spectroscopy.

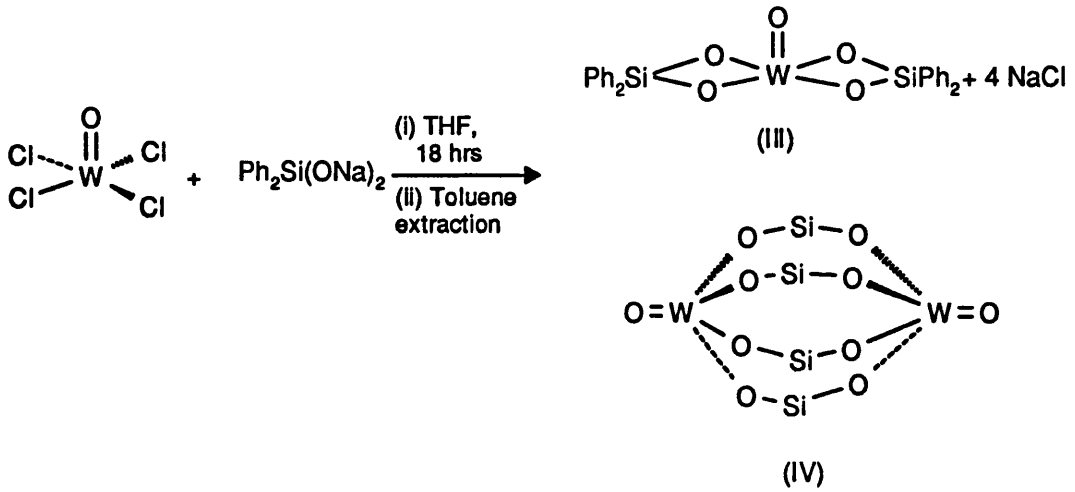


Phenyl groups on silicon omitted

Figure 39 Possible routes to eight-membered rings.[74]

These investigations into the synthesis of metallasiloxane rings began with the reaction of $[W(O)Cl_4]$ in THF with 2 equivalents of $Ph_2Si(ONa)_2$ generated *in situ*. Evaporation of the solvent followed by

toluene extraction of the resulting residue gave a white solid which can be formulated as $[WO\{OSiPh_2O\}_2]\cdot H_2O$ (P8) in 77% yield.



(III)

(IV)

Phenyl groups omitted for clarity in structure (IV)

Figure 40 Chelating and bridging structures of compound (P8)

The product formed small air and moisture sensitive needles unsuitable for a structural determination from a variety of solvents. Microanalysis and IR data of the product confirmed its hygroscopic nature.

Microanalysis	Found %	Exptd % for $[WO\{OSiPh_2O\}_2]$	Exptd % for (III)·H_2O	Exptd % for (IV)·$2H_2O$
Carbon	44.6	45.9	44.6	44.6
Hydrogen	3.75	3.21	3.44	3.44

Table 27 Microanalysis for $[WO\{OSiPh_2O\}_2]\cdot xH_2O$ (P8)

The IR data shows a sharp, intense band at 961 cm^{-1} which is typical of terminal ν(W=O) and in good agreement with other tungsten oxo halide and siloxide moieties. A second strong absorption at 916 cm^{-1} is indicative of ν(W-OSi) whilst the substituted phenyl ring vibrations can be assigned to the absorptions at 775, 741, 720 and 700 cm^{-1}. ^1H and $^{13}C\{^1H\}$ NMR spectra show well resolved resonances in the aromatic region.

Although structures of type (III) have been characterised, these normally involve smaller hetero atoms such as boron or indeed a second silicon centre. In the cases of transition metal compounds, the latter structural motif (IV) has been documented for titanium, zirconium, hafnium, tantalum and niobium centres ligated by siloxanes containing a variety of functional groups. Two eight membered metallasiloxane rings involving bridging siloxane ligands have been characterised in $[Mo(O)_2\{(O)_2Si^tBu_2\}]_2$ and $[W(N^tBu_2)_2\{(O)_2Si^tBu_2\}]_2$.[88] A twelve membered ring is also found in $[V(O)Cl\{(O)_2Si^tBu_2\}]_3$. Thus of the two postulated structures for $[W(O)\{O(SiPh_2O)\}_2]$, the latter

(IV), involving a bridging ligand would be more likely than the strained ring proposed in structure (III).

In an effort to generate an expanded metallasiloxane ring similar to $[WO\{O(SiPh_2O)_3\}_2 \cdot THF]$ (P6), a solution of $[Ph_2Si(ONa)]_2O$, generated *in situ*, was added to a suspension of $[W(O)Cl_4]$. An immediate reaction was observed, and reasonably air and moisture sensitive white needles (P9) were obtained upon toluene extraction and recrystallisation of the product from a variety of solvents.

The isolated product displayed a clean IR spectrum which closely resembled that of the oxo tungstasiloxane, compound (P6), however microanalysis and NMR spectroscopy confirmed that complete purification of the product had not been achieved.

Compound	IR data, cm^{-1}
P6	1428 $\nu(C=C)_{ring}$, 1117 ν(Si-Ph), 1076, 1028 ν(Si-O-Si), 968 ν(W=O), 918 ν(Si-O)
P9	1429 $\nu(C=C)_{ring}$, 1119 ν(Si-Ph), 1063, 1028 ν(Si-O-Si), 961 ν(W=O), 920 ν(Si-O)

Table 28 IR data for oxotungsten siloxane compounds (P6) and (P9)

2.2.4 SINGLE CRYSTAL X-RAY STRUCTURE DETERMINATION OF $[W(O)\{O(SiPh_2O)_3\}_2 \cdot THF]$ (P6)

X-ray diffraction quality crystals of (P6) were isolated from a 2:1 dichloromethane-hexane solution after storage at 0°C for 1 week. The crystals were found to be air and moisture stable and data were collected at room temperature. Relevant bond angles and distances are summarised in tables 29 and 30 respectively, further structural data (including atomic co-ordinates) are provided in appendix 1.

Compound (P6) has a monomeric structure with one molecule per asymmetric unit. The six-co-ordinate tungsten displays a distorted octahedral geometry with the oxo group *trans* to the co-ordinated THF ligand [∠O(10)-W(1)-O(9) 178.8°] in a similar arrangement to that of (WOcalix[4]arene) (146) [O-W-O 180.0°].[229] The tungsten atom is raised above the plane formed by the four equatorial chelating ligands, as is observed in the structures of $[W(O)Cl_4]$ and $[WO(OSiMe_2{}^tBu)_4]$.

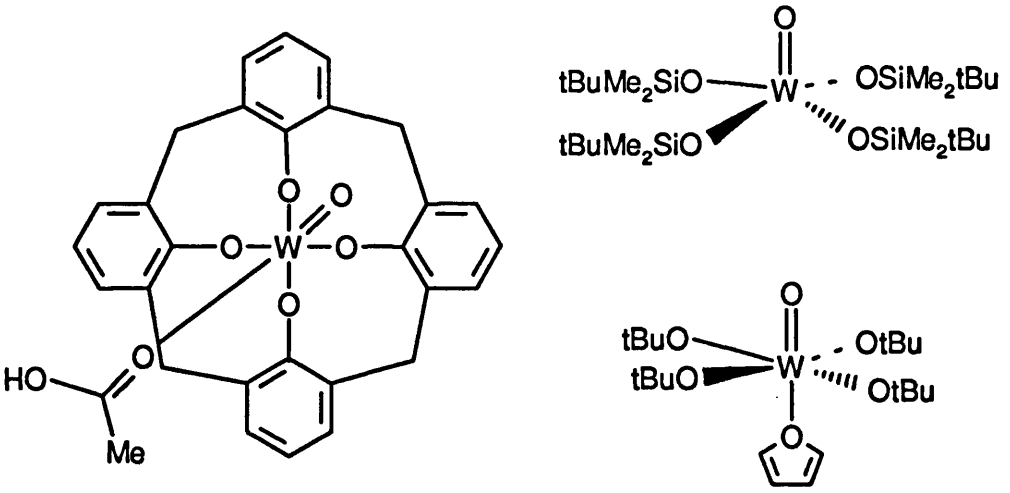


Figure 41 Structures of [WOcalix{4}arene], [WO(OSiMe$_2$^{t}Bu)$_4$] and [WO(O^{t}Bu)$_4$·THF]

The strong *trans* influence of the multiply bonded oxo ligand ensures a *trans* arrangement for the weakest π-donating ligand (THF). This is reflected in the long, [W(1)-O(9) 2.326(10) Å], bond length of the co-ordinated THF molecule in (**P6**), and that of 2.386(4) Å for the co-ordinated ethanoic acid in compound (**146**) and of THF in [WO(O^{t}Bu)$_4$·THF] (**147**).[214]

The multiply bonded oxygen distance in (**P6**) of 1.675(13) Å is typical of oxotungsten(VI) diolato species.[228] The analogous distance observed for the calix[4]arene complex is [1.698(4) Å][229] both of which are slightly shorter than those observed for mononuclear and dinuclear oxoalkoxide species [1.702(7)-1.817 Å].[230] Bond lengths are however all within the range of values for terminal oxo ligands.[231]

The W-O(Si) bond distances in (**P6**) are reasonably consistent [1.851(7)-1.896(8) Å, average 1.879 Å] and relatively short in comparison to previously characterised tungsten siloxides, 1.87-1.96 Å for [W$_2$(OSi^{t}BuMe$_2$)] and related alkene adducts, 1.889 Å for [W(N^{t}Bu$_2$)(μ-OSi^{t}BuO)$_2$]$_2$ and 1.947(4) Å for [(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_9$(O$_3$W{NMe$_2$}$_3$)].

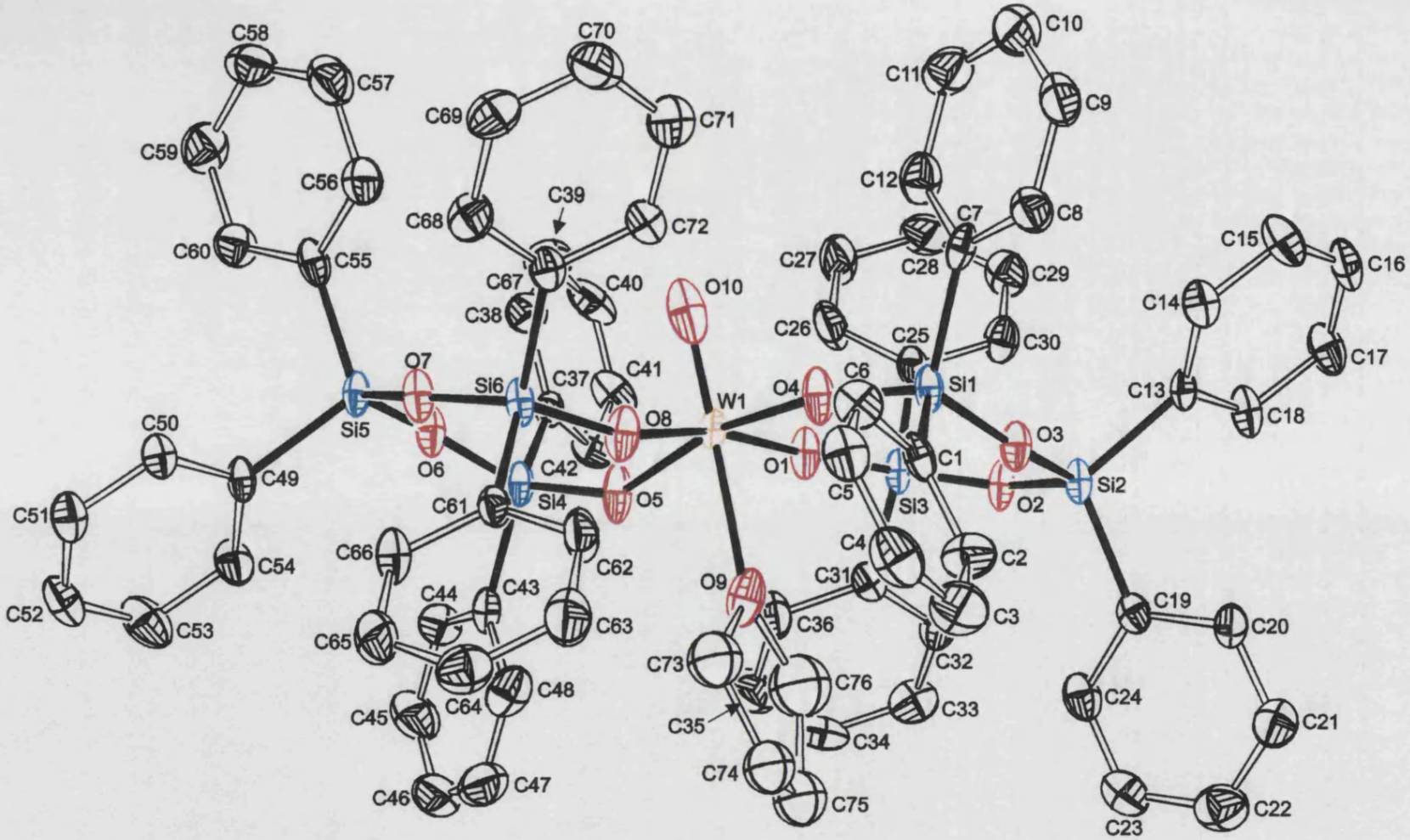


Figure 42 Molecular structure of $[WO\{O(Ph_2SiO)_3\}_2 \cdot THF]$ (**P6**)

The monomeric oxoalkoxide (**147**) which displays typical O($p\pi$)→M($d\pi$) bonding effects has W-O(R) bond lengths of 1.905(8) Å. Alcohalotatungsten(VI) complexes, for example the *cis*-dichlorobisdialato tungsten species, containing chelating diolato(2⁻) ligands displays typical W-O bond lengths of 1.874(7)-1.892(8) Å.[232] The bond distances are thus indicative of reasonably strong π-donation by the siloxide oxygen lone pairs into the empty *d*-orbitals on the metal centre.

The siloxane skeletons of the eight-membered tungstensiloxane rings lie on opposite sides of the equatorial plane of the octahedral core incorporating the tungsten atom and the chelating oxygens. Compound (**P6**) differs structurally from *cis*-[M{$O(Ph_2SiO)_3$}$(py)_2$] where M = Ti, Hf in that the eight membered rings are arranged in a *trans* disposition, as in [Sn{$O(Ph_2SiO)_3$}$_2(THF)_2$].

The average M-O-Si angles are some 5° wider than those of observed in other eight membered rings [154.3° Sn, 154.8° Ti, 153.9° Hf] and considerably larger than those (134.8°) of the six-membered oxovanadium siloxane [VO{$O(SiPh_2O)_2$}$_2$Li$(THF)_2$]. Si-O-W interbond angles are smaller than those observed for [(c-C_6H_{11})$_7Si_7O_9(O_3W\{NMe_2\}_3)$] which is presumed not to have strong π-bonding interactions between the oxygen atoms and the tungsten centre. However the relevance of bond angle data in elucidating bond characteristics has been tempered by Rothwells[233] observations suggesting that there is no direct correlation between M-O-Si bond angles and the strength of the O($p\pi$)→M($d\pi$) bonding.

The flexibility of the siloxane skeleton can be demonstrated by comparing the (Si)OWO(Si) bite angles of (**P6**) [89.9(3)° and 91.3(3)°] which are similar to those of the relatively planar eight membered [Sn{$O(SiPh_2O)_3$}$_2(THF)_2$], 90.42(7)°, and the six-membered [VO{$O(SiPh_2O)_2$}$_2$Li$(THF)_2$] of 90.1(2)°. There are notable differences to those found in the eight-membered compounds *cis*-[Hf{$O(SiPh_2O)_3$}$_2(py)_2$] 94.6(2)°, and 95.5(2)° of *cis*-[Ti{$O(SiPh_2O)_3$}$_2(py)_2$].

The tungsten atom lies outside the plane of the siloxane skeleton as in the eight-membered tin siloxane but unlike the relatively planar titanium, hafnium and vanadium species. The SiOSi angles in (**P6**) [156.2(5)-161.7(6)°] exhibit conspicuous differences with other structures, the closely related titanium [146.4(3)° and 156.0(3)°] and, hafnium [149.6(4)° and 156.6(4)°] analogues, which are smaller than those of the tin siloxane [149.09(12)° and 164.14(14)°] and close to those observed for $[Ph_2SiO]_4$, 152.3(2)° and 167.4(2)°.

O(10)-W(1)-O(1)	96.2(4)	O(3)-Si(1)-O(4)	109.5(4)
O(10)-W(1)-O(4)	96.3(4)	O(3)-Si(2)-O(2)	109.4(4)
O(1)-W(1)-O(4)	89.9(3)	O(2)-Si(3)-O(1)	111.3(4)
O(10)-W(1)-O(5)	88.4(3)	O(6)-Si(4)-O(5)	109.9(4)
O(4)-W(1)-O(5)	166.3(4)	O(6)-Si(5)-O(7)	109.4(4)
O(10)-W(1)-O(8)	96.6(4)	O(8)-Si(6)-O(7)	112.7(4)
O(1)-W(1)-O(8)	167.1(4)	Si(3)-O(1)-W(1)	169.8(5)
O(4)-W(1)-O(8)	87.4(3)	Si(2)-O(2)-Si(3)	156.2(5)
O(5)-W(1)-O(8)	91.3(3)	Si(1)-O(3)-Si(2)	159.3(6)
O(10)-W(1)-O(9)	178.8(3)	Si(1)-O(4)-W(1)	165.7(6)
O(1)-W(1)-O(9)	84.9(3)	Si(4)-O(5)-W(1)	147.9(7)
O(4)-W(1)-O(9)	84.2(4)	Si(4)-O(6)-Si(5)	161.7(6)
O(5)-W(1)-O(9)	82.1(4)	Si(6)-O(7)-Si(5)	156.5(5)
O(8)-W(1)-O(9)	82.3(3)	Si(6)-O(8)-W(1)	155.9(6)

Table 31 Selected bond angles (°) for [WO{O(SiPh$_2$O)$_3$}$_2$·THF] (**P6**)

W(1)-O(10)	1.675(13)
W(1)-O(1)	1.851(7)
W(1)-O(4)	1.872(8)
W(1)-O(5)	1.896(8)
W(1)-O(8)	1.894(7)
W(1)-O(9)	2.326(10)

Table 32 Selected bond lengths (Å) for [WO{O(OSiPh$_2$)$_3$}$_2$·THF](**P6**)

2.2.5 MOLYBDENUM SILOXIDES AND SILOXANES

A. INTRODUCTION

Molybdenum is the most prolific former of such bonds among all metals. Tungsten forms many analogous compounds but they are often more reactive, and/or less easily prepared, and for these reasons our initial interests centred on the molybdenum congeners.

Compound	Bond length (Å)	Compound	Bond length (Å)
$[Mo_2(O_2CCH_3)_4]$	2.09	$[W_2(O_2CCH_3)_4]$	2.19
$[Mo_2Cl_8]^{4-}$	2.14	$[W_2Cl_8]^{4-}$	2.25
$[Mo_2(mph)_4]$	2.07	$[W_2(mph)_4]$	2.16
$[Mo_2Cl_4(PMe_3)_4]$	2.13	$[W_2Cl_4(PMe_3)_4]$	2.26

mph = anion of 2-hydroxy-6-methylpyridine

Table 33 Representative quadruple Mo-Mo and W-W bonds and their lengths

The denser cores of the tungten atoms create significantly greater core-core repulsions than those observed in a pair of molybdenum atoms, which is consequently reflected in the Mo-Mo bond distances which are usually shorter (0.10 ± 0.04 Å) than the corresponding W-W distances.[234] As a result the δ component of the W-W bond is weakened. This is the principal reason why many quadruply bonded W_2 species are less easy to prepare and more reactive than their molybdenum analogues.

Of the many molybdenum compounds containing Mo-Mo quadruple bonds, the most useful entries to this chemistry are the carboxylate (**M6**) and the octachloro (**M7**) complexes (figure 43).

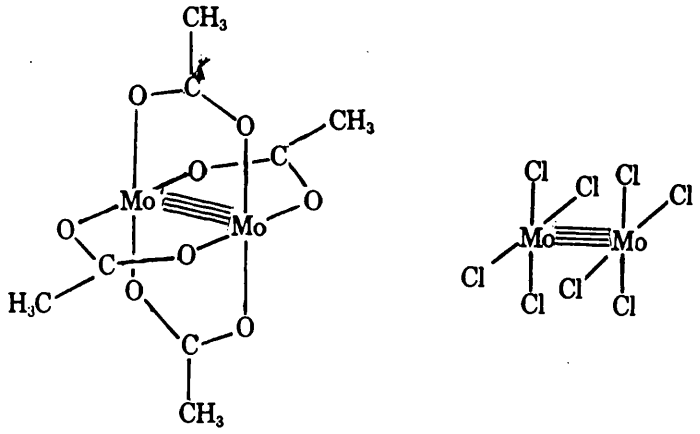


Figure 43 Quadruply bonded molybdenum carboxylate and chloride species

Among the reactions of $[Mo_2(O_2CCH_3)_4]$ and $[Mo_2Cl_8]^{4-}$ are many simple (*i.e.* non-redox) ligand-exchange reactions in which the quadruply bonded $\{Mo_2\}^{4+}$ unit remains intact (figure 44). However the carboxylate (**M6**) is less reactive than the octachloro complex (**M7**) because the paddle-wheel type structure formed by the spanning carboxylate ligands block access to the reservoir of electrons that constitute the metal-metal bond. Consequently there are few known reactions involving the carboxylate and small organic substrates.[235] Chisholm did however synthesise a number of alkoxide compounds, namely $[Mo_2(O^iPr)_4(HO^iPr)_4]$, $[Mo_2Oc\text{-Pen})_4(HOc\text{-Pen})_4]$, where *c*-Pen = cyclopentanol and $[Mo_2(OCH_2{}^tBu)_4(HNMe_2)_4]$, all containing an Mo-Mo quadruple bond.[236]

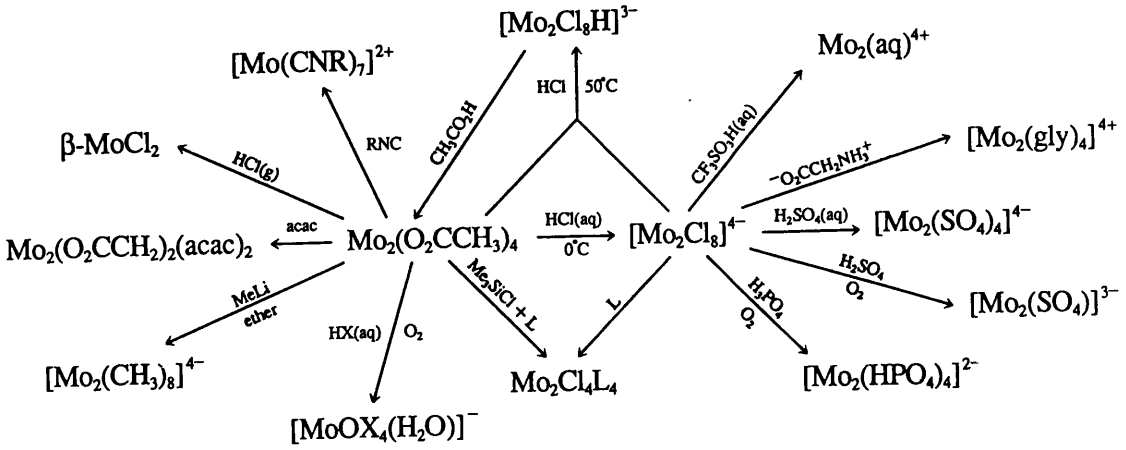


Figure 44 Ligand exchange reactions of binuclear molybdenum complexes

No known siloxides containing the M-M (M = Mo, W) quadruply bonded unit are known but Feher *et al.* prepared $[\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}_2Mo_2]$ and $[\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}_2W_2(\mu\text{-}H)(O^tBu)]$ from the reactive $[M_2(O^tBu)_6]$ unit, where M = Mo, W,[144] and Chisholm has reported in the incorporation of both alkoxides and siloxides into compounds containing a metal-metal triple bond (see section 1.3.4).

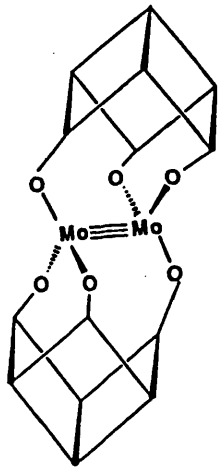


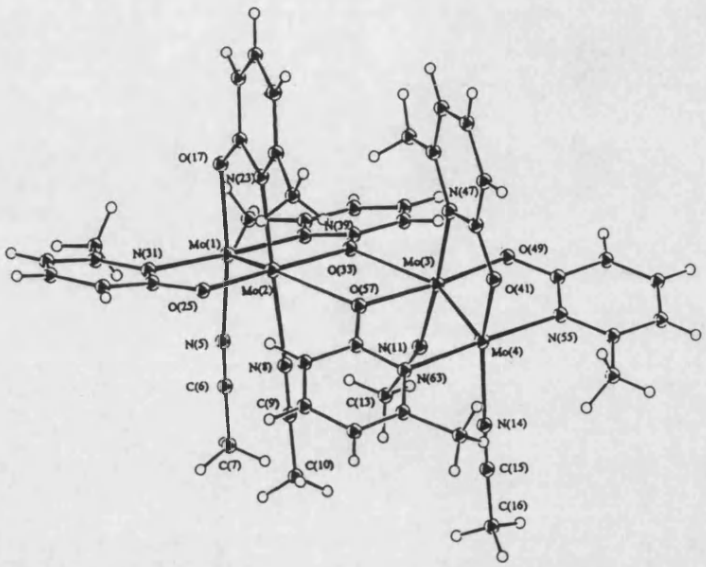
Figure 45 The structure of $[\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}_2Mo_2]$

Aside from the catalytic applications of multiply bonded transition metal compounds, the wide range of optical, magnetic, and electrochemical properties associated with such complexes has prompted a reasonably large number of additional studies.[237] These works have often centred around the production of macromolecular ordered assemblies, and in particular covalently linked, stiff-chain polymers wherein facile electron transfer is possible between quadruple bonds. Initial efforts included the synthesis of polymers containing the $\{M_2\}^{4+}$ where M = Mo, W subunit in a mixed carboxylate framework.[238]

$\{[M_2(O_2CR)_2](O_2C\text{-}R'\text{-}CO_2)[M_2(O_2CR)_2](O_2C\text{-}R'\text{-}CO_2)\}_n$ M = Mo, W; R' = oxalate, R = CF_3 **2.20**

Unfortunately polymers of this type suffered from facile carboxylate exchange reactions that often led to unselective scrambling on the M_2 cores and consequently the polymers were of limited use.

The preparation of polymers containing more kinetically persistent co-ordination spheres about the M-M quadruple bonds rested upon the development of suitable dinuclear starting materials and the selection of the ligand bridge. Chisholm reported the solvated complexes $[Mo_2(O_2C^tBu)_3(MeCN)_2]^+(BF_4^-)$ (**148**) and $[Mo_2(O_2C^tBu)_2(MeCN)_6](BF_4)_2$ to be extremely versatile reagents for the synthesis of tetranuclear complexes of the type shown in figure 46.[239]



mph = deprontated anion of 6-hydroxy-2-methylpyridine

Figure 46 Ball and stick representation of the cationic portion of $[Mo_2(mph)_3(MeCN)_2]_2^+ \cdot 2MeCN$

B. PREPARATION AND CHARACTERISATION

The binuclear molybdenum complexes, molybdenum(II) acetate, $[Mo_2(O_2CCH_3)_4]$ (**M6**) and tetrakis potassium octachloromolybdate $K_4[Mo_2Cl_8]$ (**M7**) were synthesised in good yield according to standard literature methods.[240] A slight modification was employed in the synthesis of $K_4[Mo_2Cl_8]$, a slight wash of the product with ethanol and ether removed the water of crystallisation reported in the complex from the literature preparation. Analytical data for the products was in good agreement with published results.

$$Mo(CO)_6 + \text{excess } CH_3COOH \xrightarrow[(CH_3CO)_2O]{\text{3 hr reflux}} [Mo_2(O_2CCH_3)_4] \xrightarrow[0C]{HCl/KCl} K_4[Mo_2Cl_8] \qquad \textbf{2.21}$$

Initial attempts to exchange the bridging acetate ligands with either diphenylsilanediol or sodium tetramethyldisiloxane diolate failed. Stirring THF and toluene suspensions at room temperature for prolonged periods or under reflux led only to the recovery of the original, insoluble metal carboxylate (**M6**). This outcome was not unexpected given the previously noted stability of the Mo-Mo

quadruply bonded unit, and that CH_3COOH is a stronger acid than either silanol and renders the reaction likely to suceed only if the product was soluble.

In comparison (M7) was found to undergo limited ligand substitution reactions with diphenylsilanediol and sodium tetramethyldisiloxanediolate (table 34). The high solubility of $K_4[Mo_2Cl_8]$ and silanols in polar solvents such as THF and DCM afforded an elegant separation of the products from the unreacted starting material. Pure products were obtained by simply washing the red, air sensitive solids obtained from the reactions with small portions of solvent, thus freeing the insoluble molybdenum-siloxide of the vastly more soluble starting materials. IR data and microanalysis (tables 34 and 35) of the isolated materials indicate that only partial susbstitution of the chloride ligands occurs, and to date useful NMR data have not been obtainable due to the insolubility of the products in all common solvents (MeOH, EtOH, $C_6H_5CH_3$, C_6H_6, $CHCl_3$, CH_2Cl_2, $(CH_3)_2CO$, THF, Et_2O, MeCN, H_2O).

Reagents (relative molar quantities)	Cpd	Analysis (%) C (calc)	H (calc)
$K_4[Mo_2Cl_8]$, $Ph_2Si(OH)_2$, 1:4 in toluene, stir 48 hrs	(P10)	40.3 (47.8)	3.4 (3.3)
$K_4[Mo_2Cl_8]$, $Ph_2Si(OH)_2$, 1:4 in toluene, stir 196 hrs	(P11)	17.2 (47.8)	1.6 (3.3)
$K_4[Mo_2Cl_8]$, $Ph_2Si(OH)_2$, 1:4 in toluene 91hrs, NEt_3	(P12)	3.3 (47.8)	0.9 (3.3)
$K_4[Mo_2Cl_8]$, $[Me_2Si(ONa)]_2O$ 1:4 in THF, stir 96 hrs	(P13)	6.6 (12.4)	0.8 (3.1)
$K_4[Mo_2Cl_8]$, $[Me_2Si(ONa)]_2O$ 1:4 in THF, stir 192 hrs	(P14)	4.5 (12.4)	1.0 (3.1)
$K_4[Mo_2Cl_8]$, $Ph_3Si(OH)$, NEt_3, 1:8:excess	(P16)	22.0	4.7

Table 34 Selected data for binuclear molybdenum siloxides

Cpd	IR data, cm^{-1}
(P10)	1429 ν(Si-C), 1130 ν(Si-C), 1121 ν(Si-C), 909ν(SiO-M)
(P11)	1429 ν(Si-C), 1130 ν(Si-C), 1121 ν(Si-C)
(P12)	1157 ν(Si-C), 1069 ν(SiOSi), 976 ν(SiO-M)
(P13)	1156 ν(Si-C), 1047 ν(SiOSi), 945 (SiO-M)
(P14)	1156 ν(Si-C), 1053 ν(SiOSi), 1022 ν(SiOSi), 904 ν(SiO-M)
(P16)	unobtainable

Table 35 Selected IR data for binuclear molybdenum siloxanes

Refluxing the solution containing $Ph_2Si(OH)_2$ and $[Me_2Si(ONa)_2]_2O$ led only to the recovery of the cyclic siloxanes, octaphenylcyclotetrasiloxane and octamethylcyclotetrasiloxane. Given the failure to isolate distinct and identifiable species that were soluble in any available solvent this work was discontinued.

Chapter Three: Crown Ether-Silanol Complexes

3.1 SUMMARY

A great deal of silanol and crown ether chemistry has centred on the abilities of these ligands to stabilise transition metal centres. This is reflected in the wealth of literature on these substrates as well as in the previous chapter of this thesis which examined the capability of anionic equivalents of silanols to support high oxidation state tungsten compounds. A subsequent chapter details the use of aza- and oxa- crown ethers in stabilising low oxidation state molybdenum complexes. However, the capacity of both species to form neutral, H-bonded adducts has been comparatively neglected until recently.

Investigations in this programme began with the reaction of three equivalents of Ph_3SiOH with a hot toluene solution containing 18-crown-6, which afforded after work-up $(Ph_3SiOH)_3$·18-crown-6 **(C3)** as an extremely hygroscopic powder. Attempts to produce crystals suitable for a single crystal study yielded instead the air stable compound $(Ph_3SiOH)_2$·18-crown-6·$(H_2O)_2$ **(C4)**, which has been structurally characterised. Exposure of **(C3)** to moist air resulted in a dihydrate $(Ph_3SiOH)_3$·18-crown-6·$(H_2O)_2$ **(C5)**, which was analysed by IR and microanalysis.

Addition of either one or three equivalents of triphenylsilanol to 1-aza-18-crown-6 in refluxing toluene yielded the H-bonded complex $(Ph_3SiOH)_2$·monoazacrown·H_2O **(C6)** upon slow cooling. Crystallography revealed that the triphenylsilanol molecules are attached to the crown *via* a co-ordinated water linkage and a direct SiOH···NH interaction respectively.

$(Ph_3SiOH)_2$·diazacrown **(C7)** was isolated from the reaction of two or three equivalents of triphenylsilanol with 7,16-diaza-18-crown-6 in hot toluene. A structural determination was not possible because highly disordered crystals were formed. However IR data indicates that the triphenylsilanol ligands probably bind *via* direct SiOH···NH interactions.

Solution studies using ^{29}Si NMR spectroscopy have revealed that the small changes in shift observed for the 18-crown-6 complexes **(C3)** ($\Delta\delta$ -0.8 ppm) and **(C4)** ($\Delta\delta$ -0.4 ppm) are probably to due the presence of free triphenylsilanol from the dissociated complex. The greater downfield shift ($\Delta\delta$ -2.0 ppm) of $(Ph_3SiOH)_2$·monoazacrown·(H_2O) reflects the stronger SiOH···NH interaction caused by the greater basicity of the nitrogen atom on the aza-crown. A single peak probably indicates a rapid exchange between free silanol and that co-ordinated directly to the nitrogen. Complex **(C7)** displays the largest change in chemical shift ($\Delta\delta$ -3.4 ppm) and has been attributed to the presence of two direct SiOH···NH interactions keeping the complex intact in solution.

3.2 RESULTS AND DISCUSSION

3.2.1 PREPARATION OF OXA- AND AZA- CROWN ETHER COMPLEXES

Monoaza-18-crown-6 (C1) was synthesised using a modification of the method reported by Maeda.[241] Higher yields (71%) in comparison to those noted in the literature (61%) were obtained when oligoethylene ditosylate was used rather than oligoethylene dichloride, the reaction was carried out using twice the molar equivalent of diethanolamine.

Diaza-18-crown-6 (C2) was synthesised using the method published by Kulstad and Malmsten[242] with the resultant yield (10%) being similar to that documented. Selected analytical data for (C1) and (C2) are given in table 36.

	1-aza-18-crown-6 (C1)	7,16-diaza-18-crown-6 (C2)
Microanalysis	C 54.6 (54.7), H 9.33 (9.58), N 5.20 (5.35)	C 54.8 (54.9), H 10.1(9.9), N 10.6 (10.7)
IR data (cm^{-1})	ν(N-H) 3196, ν(C-O) 1120	ν(N-H) 3320, ν(C-O) 1138
^1H NMR δppm ($CDCl_3$)	2.0 (1H, br s, N*H*), 2.79 (4H, t, CH_2HNCH_2), 3.65 (20H, m, CH_2OCH_2)	2.22 (2H, br s, CH_2NHCH_2), 2.80 (8H, t, CH_2NHCH_2), 3.61 (16H, m, CH_2OCH_2)
^{13}C NMR δppm ($CDCl_3$)	49.6 (CH_2NHCH_2) 70.3, 71.5 (CH_2OCH_2)	49.2 (CH_2NHCH_2), 70.1, 70.3 (CH_2OCH_2)

Table 36 Selected analytical data for mono- and diaza-18-crown-6

3.2.2 CROWN ETHER-SILANOL COMPLEXES

A. INTRODUCTION

The propensity of silanols, oxa- and aza-crown ethers to form, under the correct conditions, large molecular arrays and host-guest complexes has been discussed in the introductory chapter of this thesis. In both substrates the capacity to form extended hydrogen-bonded networks is determined by their polarity and the number of potential hydrogen bonding sites resident on each individual moiety. Thus it is expected that silanols, which display both high polarity and acidity, should readily form H-bonding interactions with the oxygen (or nitrogen) atoms of oxa- and aza-crown ethers.

The interest in inclusion compounds involving silanol species has remained muted despite the potential useful application of silanols as agents for the selective entrapment of alcohols from aqueous solutions as noted by Bourne.[243] Thus triphenylsilanol forms a selective host-guest compound with ethanol upon its addition to equimolar mixtures of MeOH and EtOH, PrOH and EtOH and ethanolic solutions containing up to 40% water. The crystalline adduct invariably isolated (149) has a host to

guest ratio of 4:1 and is shown in figure 47. Analogous hydrogen-bonded complexes involving the selective inclusion of dioxane have been isolated for triphenylsilanol and tri-1-naptholsilanol.[244] Weber also noted the use of the less acidic triphenylmethanol (Ph_3COH) as a highly effective sequestering agent for MeOH.[245] Further 1:1 adducts of Ph_3COH with many common solvents including acetone and DMSO were also produced. Of potential environmental importance is the series of related singly bridged triarylmethanol hosts which function as highly selective and extremely efficient sequestering agents for dioxane.[246]

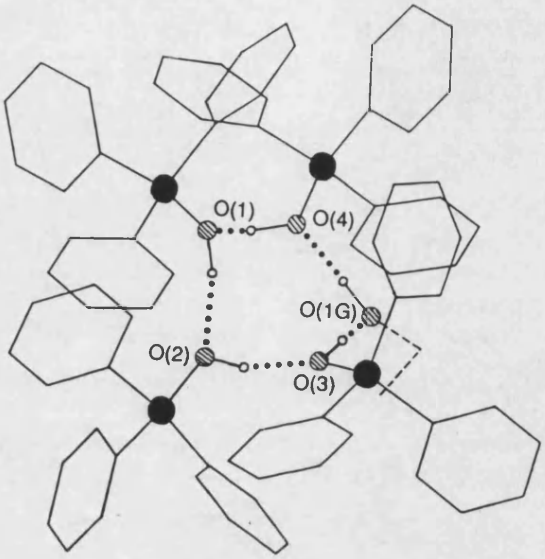


Figure 47 Perspective view of hydrogen bonding in (**149**)

An attempt to model the chemistry of complexing ligands at the sedimentary-water interface found in natural aquatic systems led to the preparation of a 2:1 strongly hydrogen bonded adduct, $(Ph_3SiOH)_2 \cdot$12-crown-4 (**150**).[253]

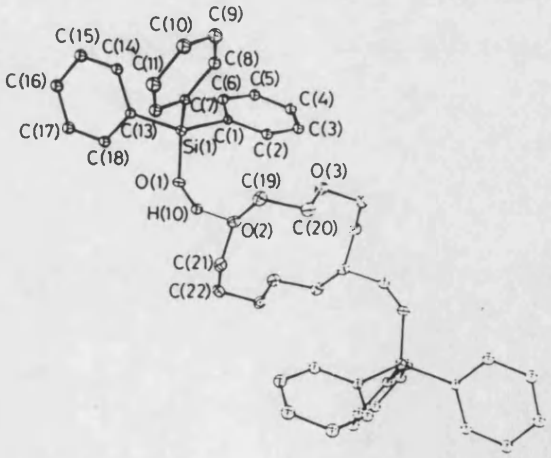


Figure 48 Molecular structure of $(Ph_3SiOH)_2 \cdot$12-crown-4 (**150**)

Complex (**150**) shows notable differences from previously characterised 18-crown-6 compounds in which an uncharged but acidic guest was attached to the host crown. The larger crown ether exhibits

a high affinity for water and in cases where the guest contains only a single proton suitable for hydrogen bonding, a complex in which the guest binds *via* an intermediate water molecule often results. Such inclusion complexes can be exemplified by the 2:1 adduct (3-nitrophenol)$_2$·18-crown-6·diaquo complex (**151**) which is probably better described as a complex between 3-nitrophenol and hydrated 18-crown-6.

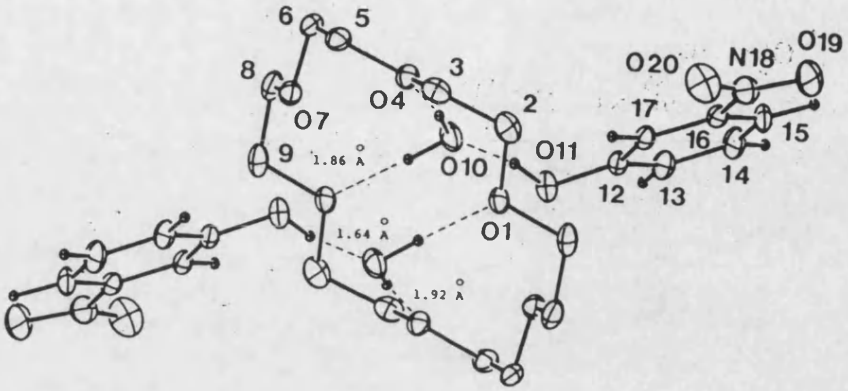


Figure 49 Molecular structure of (3-nitrophenol)$_2$·18-crown-6·(H$_2$O)$_2$ (**151**)

Similar dihydrate complexes are observed for the 2:1 adducts of 18-crown-6 with *p*-nitrobenzaldehyde oxime (**152**), 2,4-dinitrophenol (**153**), and 4,4'-biphenol (**154**). Likewise the binding of acidic guests through the mediation of co-ordinated water has been noted in the complexes (H$_2$O.HBF$_4$)$_2$.(18-crown-6) (**155**)[247] and (CCl$_3$COOH)$_2$·(18-crown-6)·(H$_2$O)$_2$ (**156**).[248] In the presence of acidic ligands protonation of the nitrogen atoms of aza-crown ethers can be observed. One of the NH_2^+ hydrogens is found to form a hydrogen bond to the water molecule centred within the macrocycle, which in addition donates its two protons to the ether oxygens.

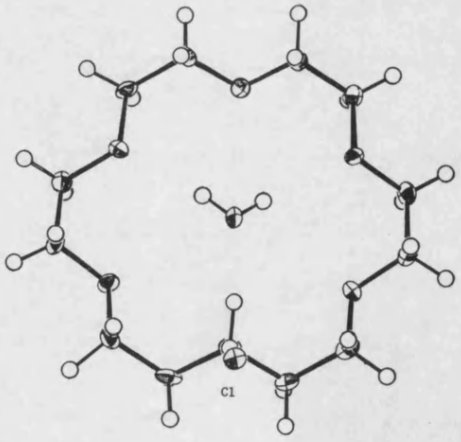


Figure 50 Molecular structure of monoaza-18-crown-6·H$_2$O·HCl

Since host-guest interactions usually take place in solution, solvation effects, and in particular the hydration of the crown ether, play an important role in stabilising the resultant complex. Exhaustive Raman and thermal analysis studies have been used to determine the degree of hydration in binary

hydrates of 18-crown-6[249] and diazacrown compounds.[250] More recent investigations have led to the structural characterisation of two binary polyhydrate complexes, 18-crown-6·6H_2O (**157**)[251] and 18-crown-6·12H_2O (**158**).[252] In this study the role of water in crown ether-silanol chemistry has been explored.

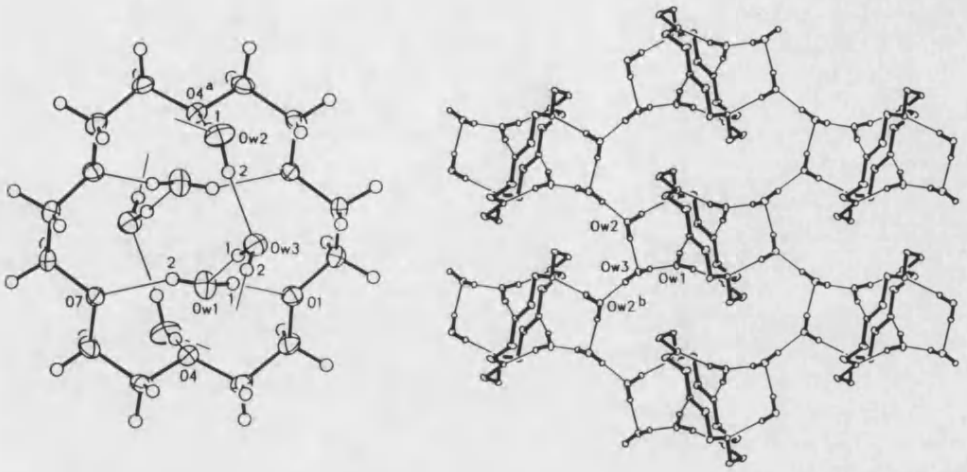
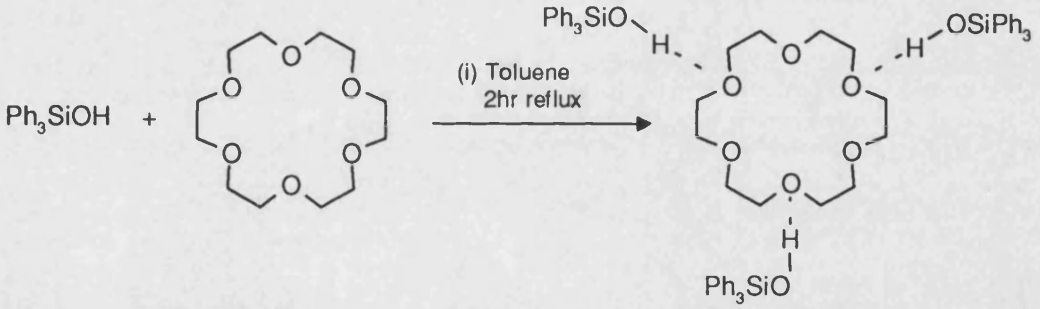


Figure 51 Molecular structures of hydrated 18-crown-6

B. PREPARATION AND CHARACTERISATION

Heating a toluene solution containing dried 18-crown-6 and three equivalents of triphenylsilanol under reflux for two hours gave ($Ph_3SiOH)_3$·18-crown-6 (**C3**) as small crystals (39%) upon reducing the volume of solvent and cooling (reaction 3.1).



3.1

The isolated complex, (**C3**) is probably analogous to the 2:1 adduct ($Ph_3SiOH)_2$·12-crown-4 (**150**)[253] in that the steric interactions between the bulky triphenylsilanol groups in (**C3**) are minimised by forming hydrogen bonds to single oxygen donor sites on the crown. A structural determination of (**150**) revealed triphenylsilanol groups binding at opposite sides of the crown (figure 48) whilst the larger crown ether in (**C3**) probably binds the guests at alternating oxygen sites. Co-ordination of the triphenylsilanol substrate to the crown ether produces noticeable changes in the position of the

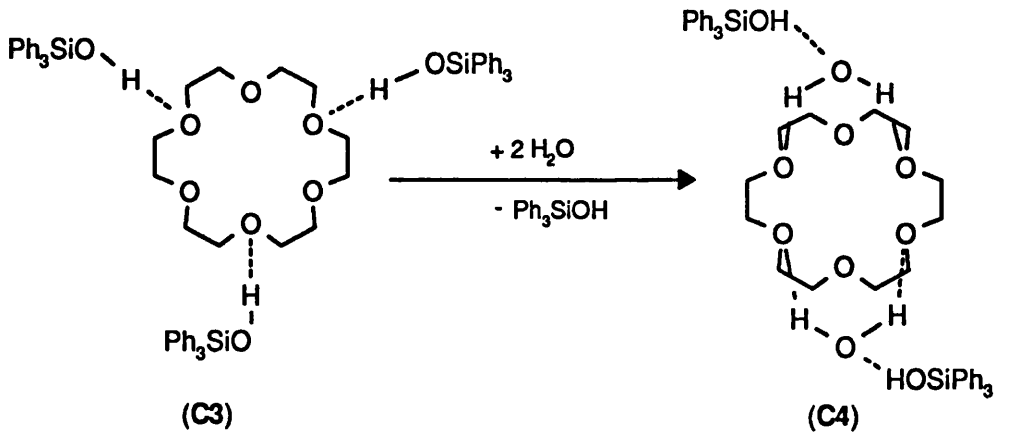
Si-OH deformation modes in the IR spectrum. Thus the H-bonded complex (**C3**) reveals a change in the observed intensities and frequencies of the δ(Si-OH) at 855 and 835 cm^{-1} in the free triphenylsilanol to an absorption at 901 (weak) and 845 cm^{-1} (strong). Intermolecular H-bonding in the crown-silanol complex ensures that the Si-OH stretching mode appears as a broad band with a slight reduction in frequency of the absorption from 3250 cm^{-1} in the uncomplexed ligand to 3200 cm^{-1} in (**C3**). Further absorptions due to the triphenylsilanol moieties occur at 1428 and 1117 ν(Si-Ph) and $\nu(C\text{-}C)_{ring}$ 741, 711 and 698 cm^{-1}. Microanalysis of the product was in good agreement with expected values (see table 37).

^{1}H NMR solution studies of (**C3**) show a singlet at 3.6 ppm corresponding to the methylene crown ether protons and two multiplets in the aromatic region (7.4 and 7.6 ppm) assigned to three equivalent triphenylsilanol ligands. Observation of only a single methylene environment is indicative of either a rapid exchange of the sites to which triphenylsilanol is bound or dissociation of the complex in solution. The latter alternative is reinforced by the presence of only a single resonance centred at -13.4 ppm in the ^{29}Si NMR spectrum. The small additional downfield shift in comparison to the free silanol (-12.6 ppm) can probably be attributed to the concentration dependent nature of ^{29}Si NMR spectroscopy and thus (**C3**) is unlikely to remain associated in solution (see also table 38).

Cpd	Microanalysis	ν(H_2O) nujol, cm^{-1}	ν(Si-OH) nujol, cm^{-1}	δ(Si-OH) nujol, cm^{-1}
(C3)	C 72.6 (72.5) H 6.65 (6.66)		3200	901, 845
(C4)	C 67.7 (67.5), H 7.16 (7.01)	3549, 3508	3206	901, 843
(C5)	C 70.1 (70.2), H 6.67 (6.79)	3550, 3501	3216	901, 841

Table 37 Selected analytical data for $(Ph_3SiOH)_x \cdot 18\text{-crown-}6 \cdot (H_2O)_x$

After compound (**C3**) was decanted from the liquor, further concentration of the filtrate and storage at -30°C produced crystals of $(Ph_3SiOH)_2 \cdot 18\text{-crown-}6 \cdot (H_2O)_2$ (**C4**) despite attempts to ensure that water was absent. The same complex was also isolated in attempts to grow crystals of (**C3**) by slow evaporation of saturated toluene solutions.



(C3) (C4) 3.2

The inclusion of water into host-guest molecules to form ternary complexes has been well documented for compounds in which the guest molecule contains only one donor atom capable of hydrogen bonding.[254] The water serves as a simple bifunctional donor with the crown, to which the guest molecule co-ordinates *via* its single donor site. Its presence in complex (C4) is consistent with the appearance in the solid of two strong, sharp ν(OH) bands at 3549 and 3508 cm^{-1} in the IR spectrum. A change in the H-bonding arrangement in the guest Ph_3SiOH is confirmed by the shift of the Si-OH deformation absorptions to 901 cm^{-1} (strong) and 843 (weak). The broad absorption at 3206 cm^{-1} is due to the Si-OH stretching frequency of the co-ordinated silanol in (C4) and is in the range characteristic of other inclusion compounds containing intermolecular H-bonding. The proposed formulation of $(Ph_3SiOH)_2 \cdot 18\text{-crown-6} \cdot (H_2O)_2$ was confirmed by microanalysis.

The ^1H NMR spectrum of (C4) shows the presence of the methylene protons of an un-coordinated 18-crown-6 at 3.7 ppm with resonances at 7.3 and 7.6 ppm due to two equivalent triphenylsilanol groups. The dissociation of complex (C4) in solution is confirmed by the ^{29}Si NMR spectrum which shows the presence of only a single signal centred at -13.0 ppm, close to that of the free silanol.

Cpd	^{29}Si NMR δ(ppm) $CDCl_3$
Ph_3SiOH	-12.6
(C3)	-13.4
(C4)	-13.0
(C6)	-14.6
(C7)	-16.0

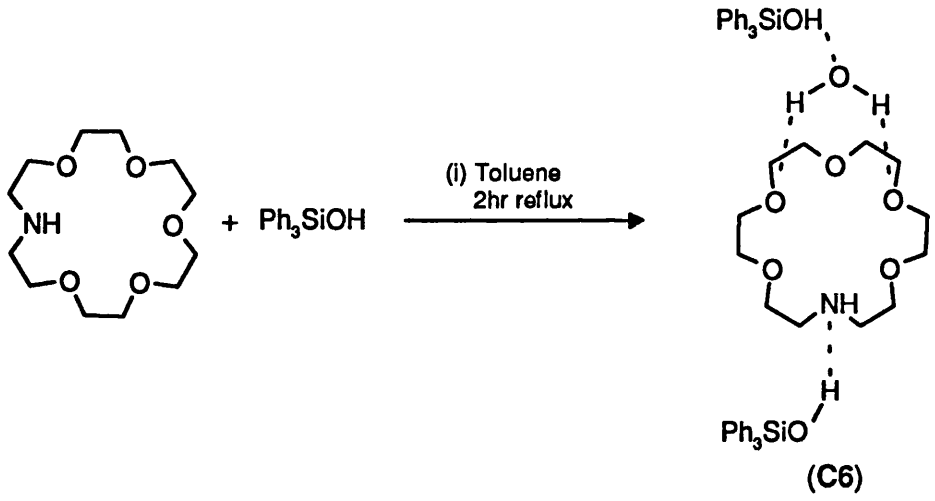
Table 38 ^{29}Si NMR data for triphenylsilanol and crown-silanol compounds.

As noted above (C3) readily incorporated water during recrystallisation to yield $(Ph_3SiOH)_2 \cdot 18\text{-crown-6} \cdot (H_2O)_2$ (C4). A structural determination of (C4) revealed an arrangement

similar to that of compounds **(151)-(156)** in which the guests bind to the crown ether molecule *via* water linkages (figure 49).

More unexpected was the high affinity of $(Ph_3SiOH)_3$·18-crown-6 for water. Exposure of powdered **(C3)** to moist air over a period of several weeks resulted in the formation of **(C5)** which microanalysis confirmed to be $(Ph_3SiOH)_3$·18-crown-6·$(H_2O)_2$. The IR spectrum of solid **(C5)** exhibits many similarities to that of $(Ph_3SiOH)_2$·18-crown-6·$(H_2O)_2$ with a broad Si-OH stretching band at 3216 cm^{-1} and weaker $\nu(H_2O)$ bands at 3550 and 3501 cm^{-1} (see table 37).

By using aza crown ethers instead of an oxa-crown it was possible to investigate the binding preferences of triphenylsilanol. Thus addition of an equimolar amount of triphenylsilanol to 1-aza-18-crown-6 in hot toluene gave $(Ph_3SiOH)_2$·1-aza-18-crown-6·H_2O **(C6)** in 53% yield upon cooling the solution to -30°C.



3.3

The IR spectrum of solid **(C6)** reveals absorptions at 3523 and 3453 cm^{-1} due to co-ordinated water. The appearance of a well defined shoulder at 3252 cm^{-1} in the IR spectrum is due to ν(N-H) of a bonded amine whilst an intense sharp Si-OH stretching band at 3135 cm^{-1} is also consistent with the formation of a direct SiOH···NH interaction.[220] A less intense broad absorption band due to Si-OH stretching remains and indicates that some intermolecular H-bonding still occurs. Si-OH deformation bands of triphenylsilanol are observed at 901 and 889 cm^{-1}, whilst phenyl absorptions occur at 745 and 710 cm^{-1}.

Cpd	Microanalysis	ν(N-H)[a]	ν(H_2O)[a]	δ(Si-OH)[a]	ν(Si-OH)[a]
(C6)	C 68.8 (69.1), H 7.25 (7.14), N 1.75 (1.69)	3252	3523, 3453	3135	901, 889
(C7)	C 70.8 (70.8), H 7.16 (7.12), N 3.36 (3.44)	3308			909, 891

a IR data recorded in cm^{-1} as nujol mulls using NaCl plates

Table 39 Selected analytical data for crown-silanol complexes

A triplet at 2.6 ppm and a quintet at 3.5 ppm in the ^1H NMR spectrum of (**C6**) show small changes in chemical shifts ($\Delta\delta$ 0.2 and 0.1 ppm respectively) in comparison with of free monoazacrown (see table 36). A small, broad singlet at 3.9 ppm is attributed to water in the complex, and two multiplets at 7.2 and 7.6 ppm are caused by the aromatic rings of triphenylsilanol. Integration of the intensities confirmed the formation of a 2:1:1 triphenylsilanol-crown-water adduct. The single absorption centred at -14.6 ppm in the ^{29}Si NMR spectrum probably indicates that dissociation of the water mediated guest, followed by rapid exchange of the silanols, occurs in solution.

A structural determination of complex (**C6**) revealed that the two triphenylsilanol groups are bound to the aza-crown through H-bonding directly with the nitrogen site and *via* water respectively (see reaction 3.3). The Si-OH···N bond distances and angles of (**C6**) are similar to those observed in the silanol-pyridazine complex, $[Ph_2Si(OH)OSi(OH)Ph_2]_3{\cdot}(C_4H_4N_2)_2$ (**159**).[258] Crystallographic studies revealed no evidence of proton transfer to yield an ammonium silanolate.

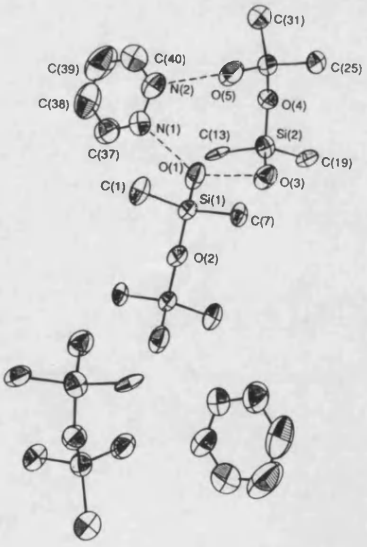


Figure 52 Molecular structure of $[Ph_2Si(OH)OSi(OH)Ph_2]_3{\cdot}(C_4H_4N_2)_2$ (**159**)

A 2:1 hydrogen bonded adduct $(Ph_3SiOH)_2$·diazacrown (**C7**) was isolated from the reaction of 2 or 3 equivalents of triphenylsilanol in refluxing solutions of diazacrown. The yield of product was inde-

pendent of the reaction stoichiometry employed with a 58% yield (based on crown) recorded upon addition of 2 equivalents of Ph_3SiOH and a slightly lower yield, 52% on using three equivalents.

Small crystals of (C7) were grown by slow evaporation of saturated toluene solutions but a satisfactory structural determination was not possible on the resultant product. Recrystallisations from a range of common solvents or the addition of water, failed to produce material suitable for crystallography.

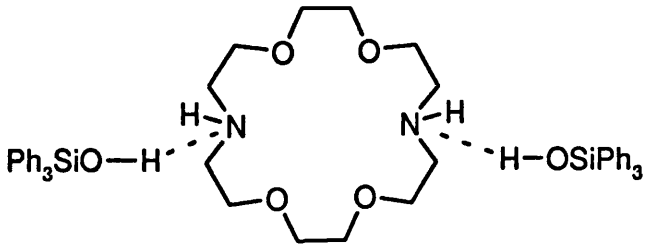


Figure 53 Expected structure of $(Ph_3SiOH)_2$·diazacrown (C7)

In contrast to the previous crown-silanol complexes, (C7) contains no water and probably binds both triphenylsilanol groups *via* strong Si-OH···H-N linkages (figure 53). A sharp absorption observed at 3308 cm^{-1} in its IR spectrum of the solid is due to ν(N-H) of a bonded amine. The corresponding reduction in intensity of the broad Si-OH stretching band at around 3200 cm^{-1} is probably the result of direct SiOH···NH interactions lessening intermolecular interactions. Bands corresponding to Si-OH deformations are shifted from 835 and 854 cm^{-1} in free triphenylsilanol to 909 and 891 cm^{-1} in the neutral adduct (C7). Microanalysis was in good agreement with the anticipated formulation of (C7) as $(Ph_3SiOH)_2$·diazacrown.

The proton NMR spectrum reveals a triplet and a quartet centred at 2.7 and 3.5 ppm respectively, characteristic of the diazacrown. Two aromatic resonances at 7.3 and 7.6 ppm indicate the presence of two equivalent triphenylsilanol groups. Whilst the changes in the ^1H NMR spectrum are too small to interpret, a considerable downfield shift to -16.0 ppm of the triphenylsilanol resonance in the ^{29}Si NMR spectrum of (C7) indicates an undissociated complex in chloroform solution.

3.2.3 SINGLE CRYSTAL X-RAY STRUCTURE DETERMINATION OF $(Ph_3SiOH)_2$·18-CROWN-6·$(H_2O)_2$ (C4)

Crystals of (C4) suitable for a structural determination were obtained from the inadvertant ingress of moisture during the slow evaporation of a toluene solution of $(Ph_3SiOH)_3$·18-crown-6 (C3). The crystals were found to be air and moisture stable and X-ray data were collected at room temperature. Relevant bond angles and distances in the resultant structure determination are summarised in tables 40 and 41. Further structural data (including atomic co-ordinates) are provided in appendix 2.

The supramolecular structure of (C4) contains an asymmetric unit consisting of one triphenylsilanol molecule, one water molecule and half of a crown ether. The 18-crown-6 host molecule is situated on an inversion centre and has pseudo-symmetry approximating D_{3d}. Two inversion related water molecules each act as hydrogen-bond donors to two crown ether oxygen atoms. Each water molecule forms a hydrogen bond with the hydroxyl group of a guest Ph_3SiOH molecule. Binding between host and guest is thus effected by bridging water molecules. The macrocyclic ring has a conformation approaching D_{3d} symmetry; bond lengths and angles are similar to those reported for 18-crown-6 in related complexes (see tables 40 and 41).[255]

In uncomplexed triphenylsilanol, the hydroxyl group is involved in intermolecular hydrogen bonding with three other molecules of Ph_3SiOH. The resultant tetrameric structure leads to Si-OH bond distances of 1.63-1.65 Å and intermolecular O···O contacts of 2.64-2.68 Å.[3] In complex (C4), the hydroxyl group participates in intermolecular O-H···O(water) hydrogen bonding. The hydrogen bond O(4)-(H4)···O(5) of (C4) is shorter (1.82 Å) than that observed in the $(Ph_3SiOH)_2$·12-crown-4 adduct (1.91 Å) and nearly linear (170°). The O···O bond distance [O(4)-O(5) 2.72 Å] is similar to those observed for a number of silanol inclusion compounds, *e.g.* $(Ph_3SiOH)_4$·dioxane (2.70 and 2.79 Å), $(Ph_3SiOH)_2$·12-crown-4 (2.76 Å), $(Ph_3SiOH)_4$·EtOH (2.60-2.79 Å) and [(1-naphthyl)$_3$SiOH]·dioxane (2.74 Å) as well as the 1:1 adduct Ph_3COH·MeOH (2.71 and 2.72 Å) and the 2:1 adduct with DMSO (2.84 Å).

Complex (C4) provides another example of a substrate (guest) molecule which binds to host sites through the mediation of water molecules. The hydrogen bonds between the protons of the water and the ether oxygens on the host are somewhat longer [H(5)-O(2) 2.08 Å and H(6)-O(3) 2.22 Å] than between the guest and water. However they are similar to those of (2,4-dinitrophenol)$_2$·18-crown-6·$(H_2O)_2$ [2.05 and 2.22 Å], but longer than those noted in (3-nitrophenol)·18-crown-6·$(H_2O)_2$ [1.86 and 1.92 Å].

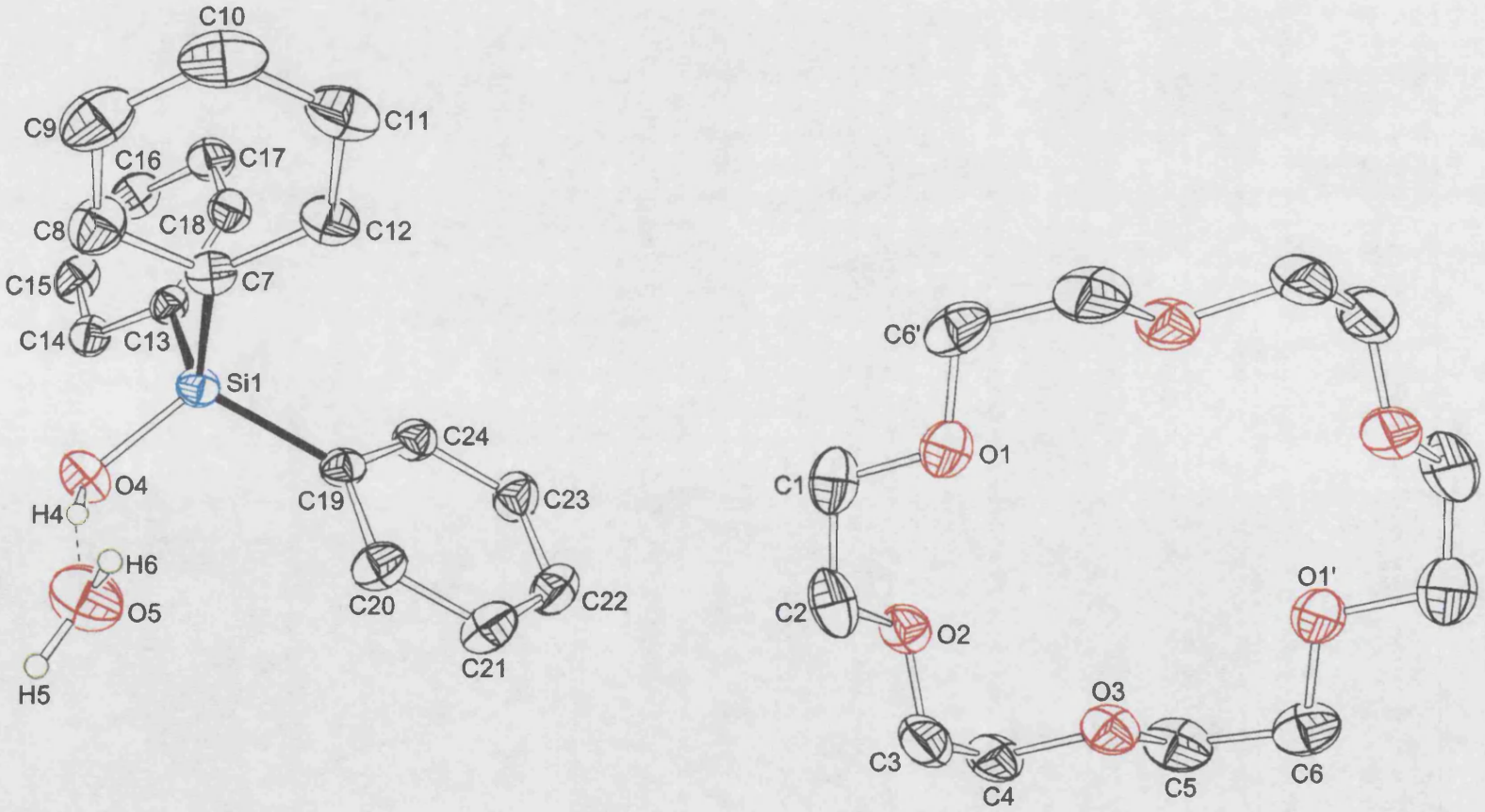


Figure 54 Molecular structure of $(Ph_3SiOH)_2 \cdot 18\text{-crown-6} \cdot (H_2O)_2$ **(C4)**

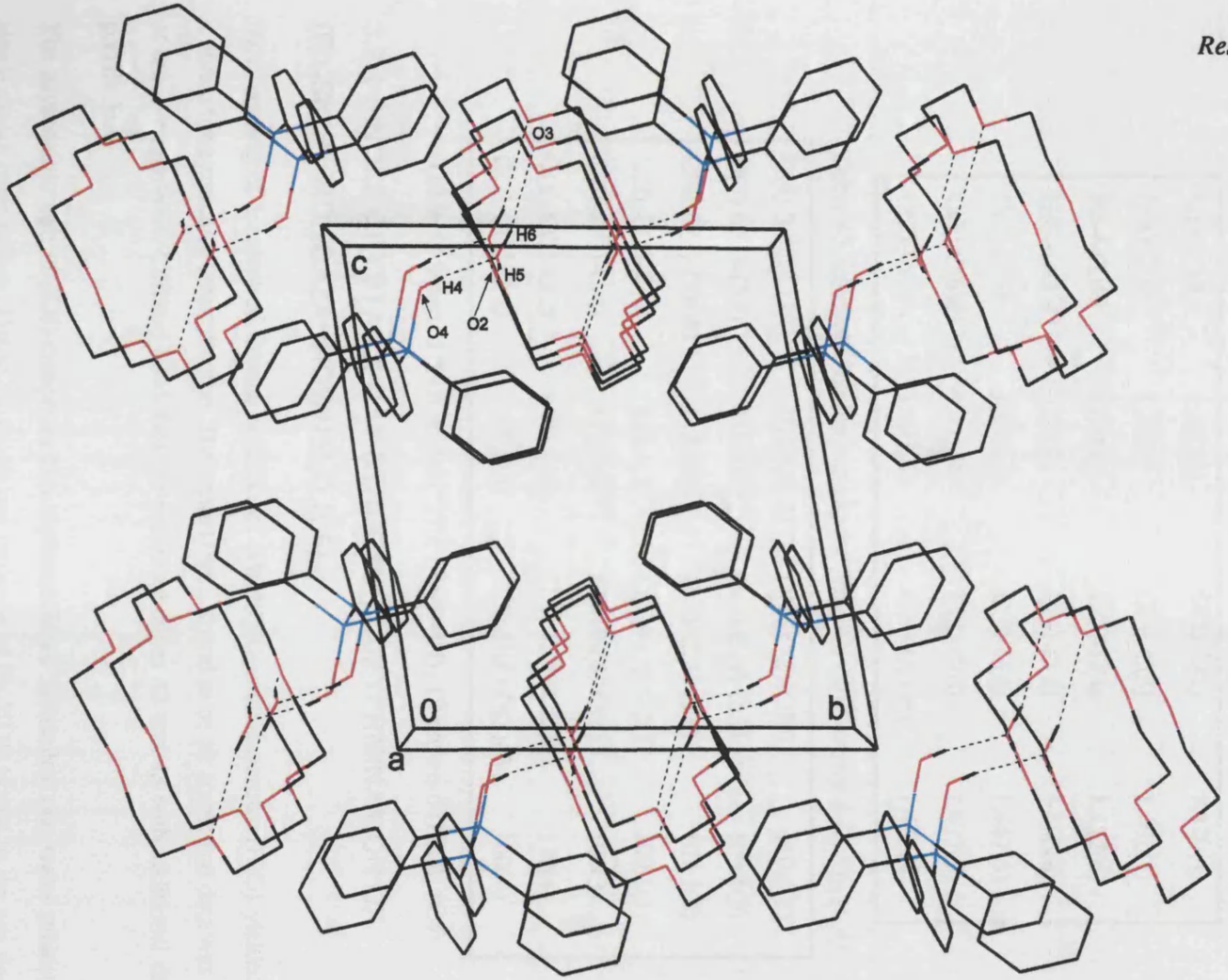


Figure 55 Supramolecular structure of $(Ph_3SiOH)_2 \cdot 18\text{-crown-6} \cdot (H_2O)_2$ **(C4)**

In contrast to the substituted phenol compounds, $(Ph_3SiOH)_2$·18-crown-6·$(H_2O)_2$ exhibits supra-molecular structure in which discrete hydrogen-bonded units are formed by the combination of intra- and inter- molecular contacts of the guest-water and water-host bonds. Figure 54 shows the units to consist of a crown ether moiety and its associated water molecules sandwiched between two offset triphenylsilanols, which when viewed at a more oblique angle show alignment of the crown ether moieties (figure 55).

Si(1)-O(4)	1.620(2)	O(2)-C(2)	1.420(4)
H(4)-O(5)	1.82(3)	O(3)-C(5)	1.402(4)
H5-O(2)#2	2.08(3)	O(3)-C(4)	1.422(4)
H(6)-O(3)#3	2.22(3)	C(1)-C(2)	1.480(6)
O(1)-C(1)	1.393(4)	C(3)-C(4)	1.467(5)
O(1)-C(6)#1	1.413(4)	C(5)-C(6)	1.477(5)
O(2)-C(3)	1.393(4)	C(6)-O(1)#1	1.413(4)

Table 40 Selected bond lengths (Å) for $(Ph_3SiOH)_2$·18-crown-6·$(H_2O)_2$ **(C4)**

O(4)-Si(1)-C(13)	107.60(12)	O(2)-C(3)-C94)	110.4(3)
O(4)-Si(1)-C(7)	110.23(12)	O(3)-C(4)-C(3)	109.4(3)
C(1)-O(1)-C(6)#1	112.8(3)	O(3)-C(5)-C(6)	109.1(3)
C(3)-O(2)-C(2)	113.1(3)	O(1)#-C(6)-C(5)	109.1(3)
C(5)-O(3)-C(4)	113.2(3)	O(4)-H(4)-O(5)	170(3)
O(1)-C(1)-C(2)	108.5(3)	O(5)-H(5)-O(2)#2	170(4)
O(2)-C(2)-C(1)	109.8(3)	O(5)-H(6)-O(3)#3	160(4)

Table 41 Selected bond angles (°) for $(Ph_3SiOH)_2$·18-crown-6·$(H_2O)_2$ **(C4)**

3.2.4 SINGLE CRYSTAL X-RAY STRUCTURE DETERMINATION OF $(Ph_3SiOH)_2$·MONOAZACROWN·H_2O (C6)

Slow cooling of a saturated toluene solution of $(Ph_3SiOH)_2$·monoazacrown·(H_2O) yielded crystals suitable for a structure determination. The crystals were found to be air stable and data was collected at room temperature. Collated bond data are presented tables 42 and 43 with additional data in appendix 3.

The asymmetric unit of (C6) comprises two triphenylsilanol molecules, one water molecule and a single crown ether moiety. Figure 56 shows one molecule of Ph_3SiOH bound to the aza crown ether through a hydrogen bond from the hydroxyl group of the silanol to the nitrogen atom of the crown. The second silanol moiety is attached *via* a water molecule co-ordinated to the aza crown through the

interaction of the hydrogen atoms of the water with the oxygen atoms of the aza crown on the opposite side to the nitrogen atom. The supramolecular structure (figure 57) is built up of discrete hydrogen bonded entities in which each crown and its associated water molecule is sandwiched between two triphenylsilanols.

The crown ligand adopts a conformation similar to that observed in the inclusion compound monoazacrown·H_2O·HCl (**160**)[256] and in the protonated crown-organometallic complex (H^+monoazacrown)$_2$[$SnCl_5(H_2O)]_2$·H_2O·MeCN (**161**).[257] In complex (**C6**) both hydrogen atoms of the water molecule participate in hydrogen bonding [H(8B)-O(4) 2.11 Å and H(8B)-O(6) 2.22 Å]. A triphenylsilanol molecule is bound to the aquo monoazacrown *via* a H-bond between the oxygen atom water molecule and the hydroxyl group of the silanol moitey [O(1)-H(1A)···O(8#1) 1.95 Å, 180°]. The interaction is probably weaker than that observed in the slightly bent linkage [1.82 Å, 170°] of $(Ph_3SiOH)_2$·18-crown-6·$(H_2O)_2$ or in the binary complex $(Ph_3SiOH)_2$-12-crown-4 [1.91 Å]. The Si-O bonds [Si(1)-O(1) 1.63 Å and Si(2)-O(2) 1.61Å] remain essentially unchanged from the uncomplexed silanol [1.62-1.65 Å] and similar to those in $(Ph_3SiOH)_2$·18-crown-6·$(H_2O)_2$ [1.62 Å].

The second triphenylsilanol group is linked *via* a hydrogen bond between the hydroxy group of the silanol and the nitrogen atom of the crown ether. Complex (**C6**) represents the first structurally characterised compound displaying a hydrogen bond between a silanol and an aza-crown. The relatively strong and nearly linear linkage [H(2A)-N(1) 1.95 Å, 167°] is similar to that of the other coordinated triphenylsilanol moiety *vide supra*. The O···N distance of [O(2)-N(1) 2.77 Å] and is close to those observed in the adducts $[(Ph_2SiOH)_2O]_3$·$2C_4H_4N_2$ [O···N 2.75 Å][258] and 1,10-diaza-18-crown-6·8.5H_2O [N···O_{water} 2.75 Å] and similar to that of the silanol-oxygen hydrogen bond found in $(Ph_3SiOH)_2$·12-crown-4 [2.76 Å]. N-H [N(1A)-O(8#1) 1.95 Å] and Si-O [Si(1)-O(1) 1.63 Å and Si(2)-O(2) 1.61 Å] bond distances are also in good agreement with calculated values observed for the interaction of ammonia and pyridine on silica surfaces.[259]

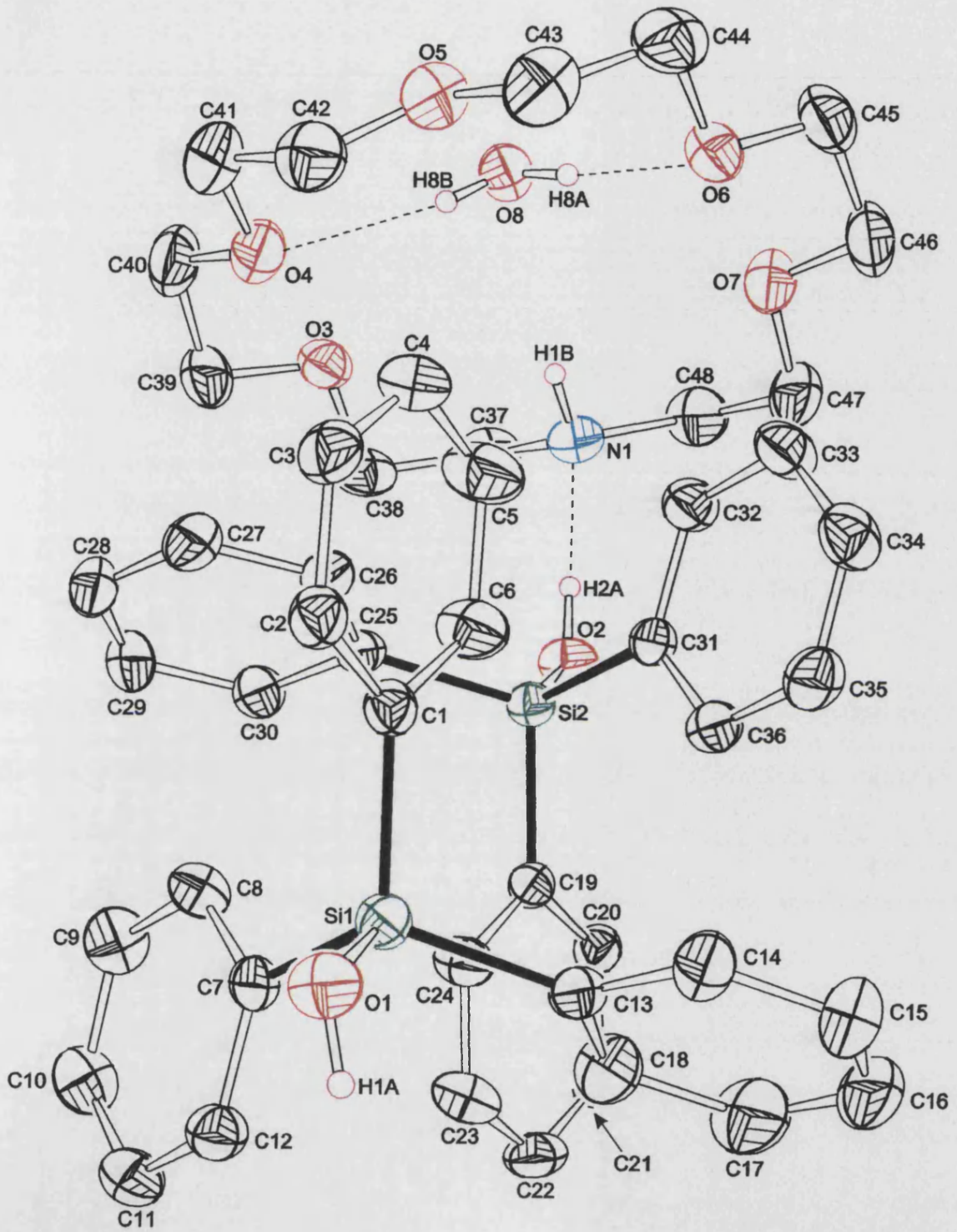


Figure 56 Molecular structure of $(Ph_3SiOH)_2$·monoazacrown·(H_2O) (**C6**)

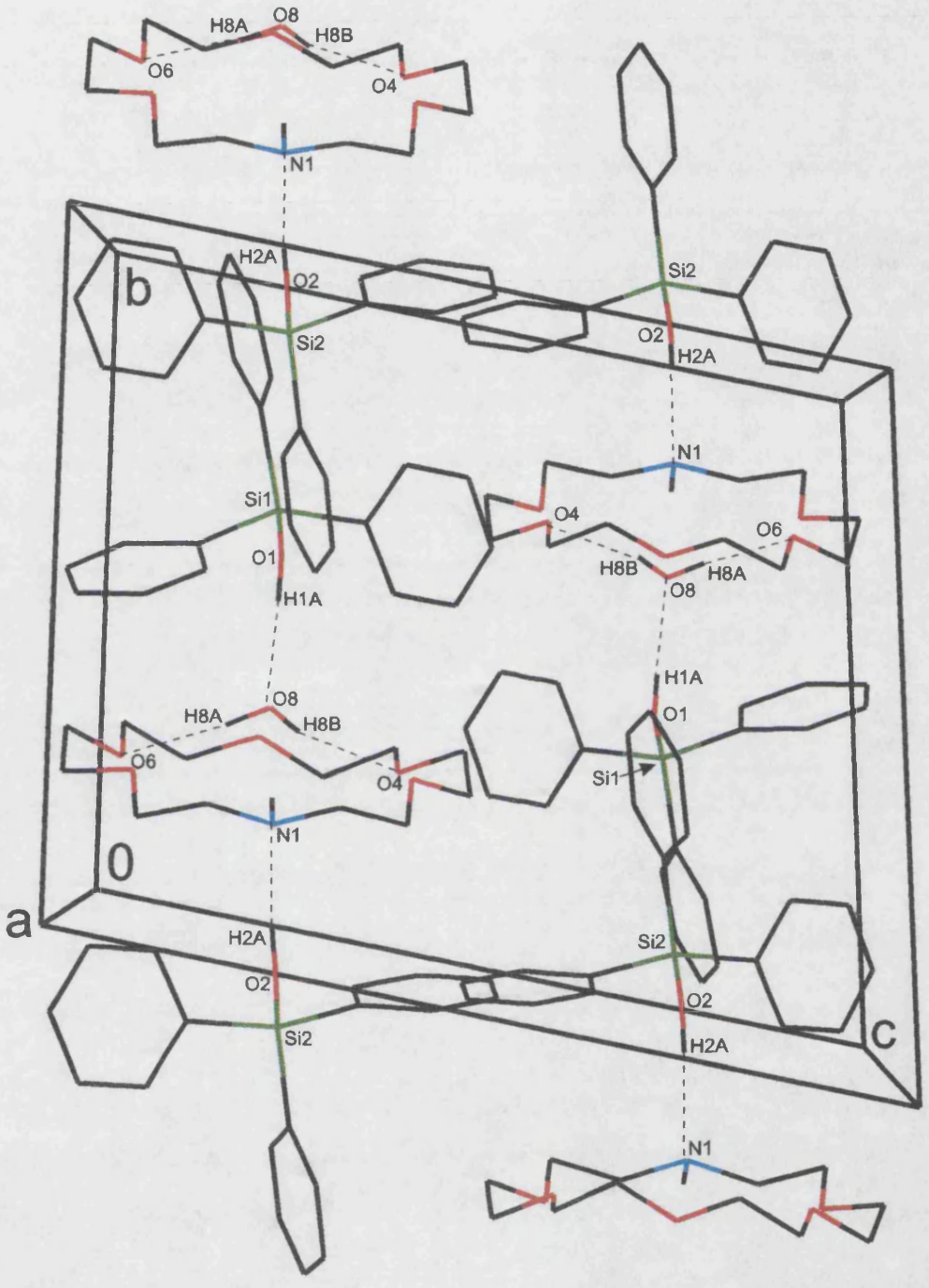


Figure 57 Supramolecular structure of $(Ph_3SiOH)_2$·monoazacrown·(H_2O) **(C6)**

Si(1)-O(1)	1.625(2)	O(5)-C(42)	1.405(4)
Si(2)-O(2)	1.613(2)	O(6)-C(45)	1.395(4)
N(1)-C(37)	1.455(4)	O(6)-C(44)	1.412(4)
N(1)-C(48)	1.471(4)	O(7)-C(47)	1.408(4)
O(3)-C(39)	1.400(4)	O(7)-C(46)	1.409(4)
O(3)-C(38)	1.416(4)	H(1A)-O(8#1)	1.95(2)
O(4)-C(41)	1.401(4)	H(2A)-N(1)	1.95(2)
O(4)-C(40)	1.414(4)	H(8B)-O(4)	2.11(2)
O(5)-C(43)	1.392(4)	H(8A)-O(6)	2.22(2)

Table 42 Selected bond lengths for $(Ph_3SiOH)_2$·monoazacrown·H_2O (**C6**)

N(1)-C(37)-C(38)	112.0(3)	O(6)-C(45)-C(46)	109.9(3)
O(3)-C(38)-C(37)	108.7(3)	O(7)-C(46)-C(45)	109.4(3)
O(3)-C(39)-C(40)	109.6(3)	O(7)-C(47)-C(48)	108.7(3)
O(4)-C(40)-C(39)	109.4(3)	N(1)-C(48)-C(47)	112.7(3)
O(4)-C(41)-C(42)	109.1(3)	O(1)-H(1A)-O(8#1)	180(3)
O(5)-C(42)-C(41)	108.9(3)	O(2)-H(2A)-N(1)	167(3)
O(5)-C(43)-C(44)	109.3(3)	O(8)-H(8B)-O(4)	167(3)
O(6)-C(44)-C(43)	109.2(3)	O(8)-H(8A)-O(6)	173(3)

Table 43 Selected bond angles for $(Ph_3SiOH)_2$·monoazacrown·H_2O (**C6**)

Chapter Four: Crown Supported Molybdenum Complexes

4.1 SUMMARY

Previous studies have shown molybdenum(II) η^3-allyl complexes of the type $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$ (M8) to be catalytically active in alkyne oligomerisations. In solution autoionisation of (M8) results in the formation of an equilibrium consisting of the cationic $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_3]^+$ moiety, and the anionic $[MoCl_{1.5}(\eta^3\text{-}C_3H_5)(CO)_2]_2^-$ species, see reaction 4.1.

$$3\,[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_3] \rightleftharpoons [Mo(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_3]^+ + \left[(CO)_2(\eta^3\text{-}C_3H_5)Mo\begin{smallmatrix}Cl\\ \diagup\\ Cl\\ \diagdown\\ Cl\end{smallmatrix}Mo(\eta^3\text{-}C_3H_5)(CO)_2\right]^- + 3\,MeCN \qquad \textbf{4.1}$$

Studies indicate that it is the former, cationic species which is the catalytically active constituent. Thus this study attempted to stabilise a cationic $[Mo(\eta^3\text{-}C_3H_5)(CO)_2]^+$ species by replacing the neutral MeCN and Cl^- ligands of (M8) with oxygen and nitrogen containing macrocycles. It was anticipated that subsequent investigations of the catalytic cycle could then be used to irrevocably establish the active entity.

Attempts to support a molybdenum allyl dicarbonyl entity using 18-crown-6 and monoazacrown macrocycles were unsucessful, generating instead, intractable oils from which no solid could be recovered. However, reaction of warmed acetonitrile solutions of (M8) with equimolar amounts of diazacrown produced the insoluble host-guest complex $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)]_2$·diazacrown (**MC1**). An earlier one pot synthesis involving (M8), 1,4,7-triazacyclononane and NH_4PF_6 (or KPF_6) had led to the replacement of the chloride, and both acetonitrile ligands in yielding the air stable complex $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(triazacrown)]^+PF_6^-$ (**MC5**). These reactions highlight the preference of low oxidation state molybdenum species to form stable complexes through binding to the "softer" nitrogen donors of the aza- crown and crown ether macrocycles.

Alternative synthetic strategies were employed in an attempt to generate complexes displaying either 1:1 host-guest stoichiometry and greater solubility in common organic solvents. Reaction of toluene solutions containing $Mo(CO)_6$ and $CF_3COOC_3H_5$ with equimolar amounts of 18-crown-6 and, di-

azacrown again produced intractable oils from which no solid could be isolated. In the latter case protonation of the crown by the allyl trifluoroacetate moiety resulted in the isolation of $(H_2\cdot\text{diazacrown})^{2+}\cdot(CF_3COO)_2^{2-}$.

Molybdenum allyl dicarbonyl complexes may also be formed *via* isolable $[Mo(CO)_4(L)_2]$ intermediates, where L = bidentate ligand, which are generated by direct combination of $Mo(CO)_6$ with the ligand. Attempts to replicate this methodolgy led to the isolation of $[Mo_2(CO)_6\cdot\text{diazacrown}]$ **(MC2)** from the addition of an equimolar amount of diazacrown to a refluxing toluene solution of $Mo(CO)_6$. Identification of the metal entity as either two independent $Mo(CO)_3$ units or a single metal-metal mutiply bonded $[Mo_2(CO)_6]$ unit was not achieved due to the low solubility of **(MC2)** in all common solvents with which it did not react. Attempts to generate analogous chromium and tungsten complexes proved unsuccessful. However, $[Mo(CO)_4(\text{diazacrown})]$ **(MC4)** was successfully isolated by displacement of bicycloheptadiene from $[Mo(CO)_4(C_7H_8)]$ **(M9)** using a dichloromethane solution of diazacrown.

4.2 INTRODUCTION

4.2.1. TRANSITION METAL-ALLYL COMPLEXES

Transition metal η^3-allyl complexes find great utility as catalysts in the synthesis of organic molecules. In particular they have proven to be a powerful and versatile reagent for the formation of highly specific organic molecules *via* the creation of new carbon-carbon bonds. Their ability to selectively react with both nucleophiles and electrophiles has been exhaustively explored since the first η^3-allyl transition metal complex, $[Co(CO)_3(\eta^3\text{-}MeC_3H_4)]$ **(162)**, was prepared in 1958 by Jonassen.[260] Thus isolation of the cobalt complex **(162)** from the reaction of potassium tetracarbonylcobaltate, glacial acetic acid and butadiene, initiated a range of studies, which in subsequent years has led to the preparation of η^3-allyl complexes for nearly all the transition metals. In turn their potential in organic synthesis has been realised and continues to drive further investigations, even today.

A. PREPARATIVE ROUTES

There are a wide variety of strategies that can be employed to form transition metal η^3-allyl complexes, the more typical routes shown below.

(i) Reaction of allylic compounds with transition metal complexes

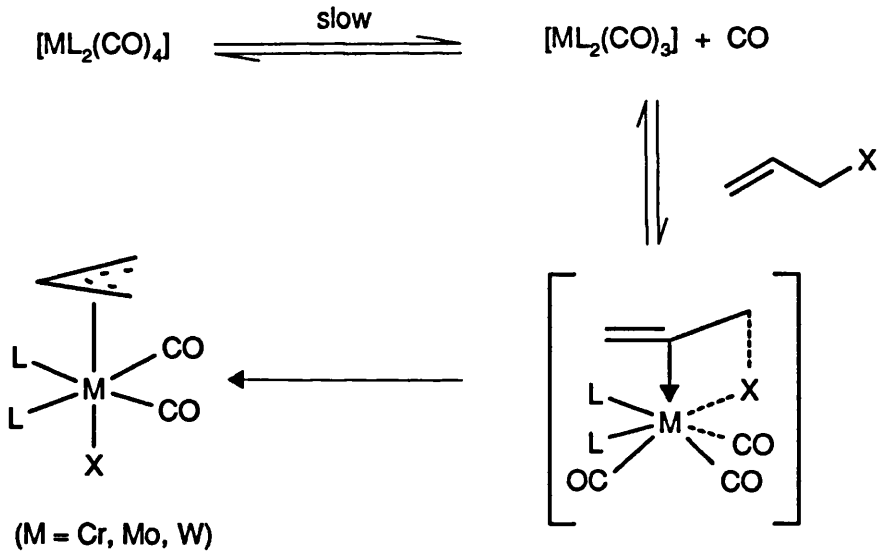
The reaction of allyl halides with low valent transition metal complexes is probably the most widely used route for the preparation of η^3-alkyl complexes.[261]

$$[Mo(NCMe)_3(CO)_3] + H_2C{=}CHCH_2Cl \xrightarrow[-\ MeCN]{-\ CO} [MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$$

$$[W(CO)_3(py)bipy)] + C_3H_5Cl \xrightarrow{-\ CO} [WCl(\eta^3\text{-}C_3H_5)(bipy)(CO)_2] + \text{pyridine} \qquad \textbf{4.2}$$

Common features of these reactions are the displacement of a previously co-ordinated ligand (*e.g.* CO), an increase of two in the metal oxidation state and, as the allyl unit formally occupies two co-ordination sites, an increase in the metal co-ordination number.

The mechanism of the oxidative addition of allyl compounds to the tetracarbonyl complexes of Group VIB metals, $[ML_2(CO)_4]$ (M = Cr, Mo, W), is thought to proceed *via* an initial rate determining step involving the dissociation of a carbon monoxide ligand. Co-ordination of the allyl compound to the zero valent metal is then followed by further elimination of CO affording the η^3-allyldicarbonyl complex following oxidative addition (scheme 14).[262]



Scheme 14 Mechanism of oxidative addition for $[ML_2(CO)_4]$

The more nucleophilic metal carbonyl anions, $[CpMo(CO)_3]^-$ and $[CrCl(bipy)(CO)_3]^-$ react with allyl halides to form the corresponding η^3-allyl complexes.[263] Protonation of mixtures of arenetricarbonyl complexes (M = Cr, Mo, W, Fe) with allyl alcohol, using hydrofluoroboric acid also results in η^3-allyl complexes (reaction 4.3).[264]

$$[M(CO)_6] + H_2C{=}CHCH_2OH + HBF_4.Et_2O \xrightarrow{h\upsilon} [Mo(\eta^3\text{-}C_3H_5)(CO)_5]^+BF_4^- \qquad \textbf{4.3}$$

Other preparative schemes include Alpers', and later Gibsons' use of two phase transfer catalysis, Rosans' dehydration of allylic alcohols or *via* protonation of co-ordinated dienes.[263] Finally, Hill reported that photoreaction between $[CpMX(CO)_3]$ where M = Mo, X =Cl; M = W, X = Cl, I, and allylic halides leads to the corresponding η^3-allyl complexes.[265]

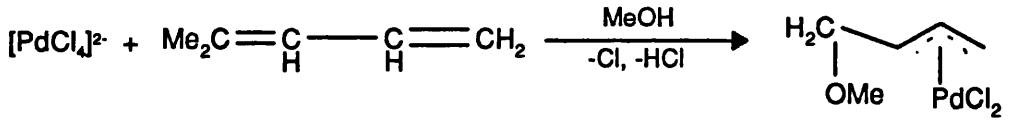
(ii) Reaction of allyl Grignard reagents with transition metal halides

Allyl Grignard reagents,[266] and less commonly, allyl-lithium and other main group allyl reagents,[267] react with certain anhydrous metal (M = Mo, Ti) halides to produce η^3-allyl complexes *via* an intermediate η^1-allyl complex (reaction 4.4).

$$[Mo(\eta^6\text{-}C_6H_6)Cl(\eta^3\text{-}C_3H_5)]_2 + 2\ C_3H_5MgCl \longrightarrow [Mo(\eta^6\text{-}C_6H_6)(\eta^3\text{-}C_3H_5)_2] + 2\ MgCl_2 \qquad 4.4$$

(iii) Reaction of 1,3-dienes or alkynes with transition metal complexes

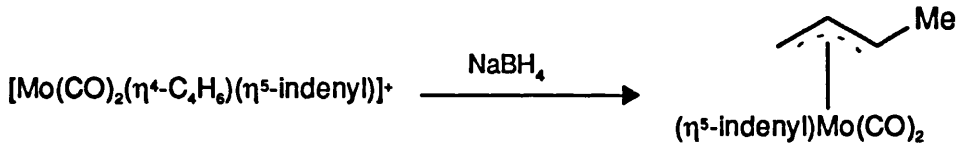
Transition metal η^3-allyl complexes can be successfully prepared *via* the insertion of 1,3-dienes[260] and alkynes[268] into transition metal hydride or alkyl complexes. Metal anions can also be reacted with dienes or alkynes to give η^3-allyl complexes (reaction 4.5).[263]



4.5

(iv) Reaction with unco-ordinated dienes or alkynes

η^3-allyl complexes may be prepared by direct protonation with an acid, or *via* nucleophilic attack upon a co-ordinated diene by H^-, OR^- or R^- (reaction 4.6).[263]

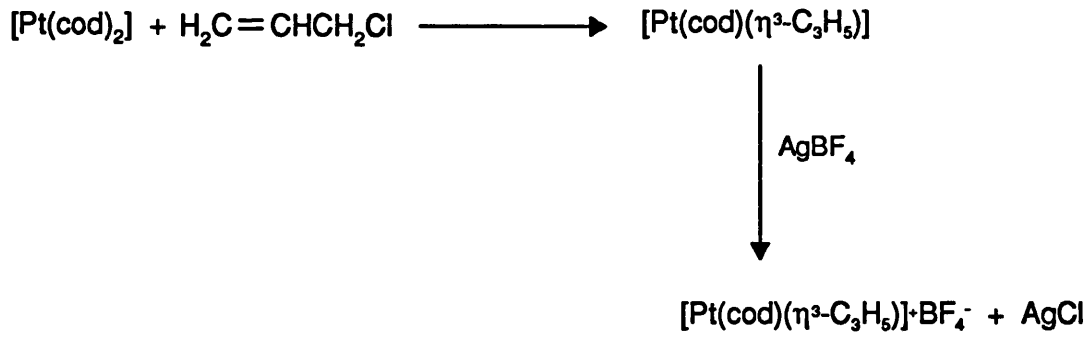


4.6

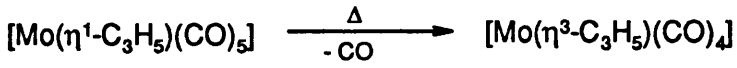
(v) Conversion of η^1-allyls to η^3- allyl complexes

Chemical,[269] thermal[270] and photochemical[271] methods have been used to prepare η^3-allyl complexes from isolable η^1-allyls via the loss of two electrons from the metal co-ordination sphere (scheme 15). In many reactions, the η^1-allyls are frequently postulated as unstable intermediates in η^3-allyl formation.

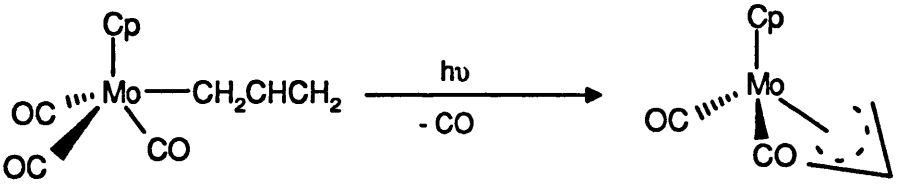
- Chemical method (halide extraction)



- Thermolysis



- Photolysis



Scheme 15 Conversion of η^1-allyl to η^3-allyl complexes

B. BONDING EFFECTS

The allyl group can bind in one of two ways; the monohapto-form (I), in which case it is a simple $1e^-$ X-type ligand, and the trihapto form (II), in which case it acts as a $3e^-$ ligand. It is possible to depict (II) in terms of the resonance forms (IIa) and (IIb) (figure 58).[272]

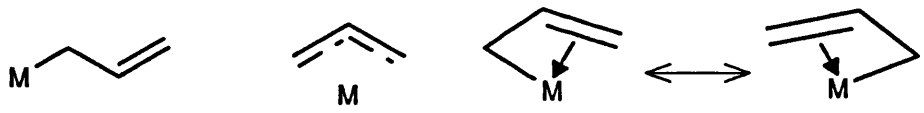


Figure 58 Binding arrangements of the allyl (C_3H_5) ligand

Usually both (IIa) and (IIb) contribute equally to the final structure and as a result both C-C distances are equal. However when the ligands *trans* to the allyl group have very different *trans* effects, the C-C distances can become unequal. For example, in [MoCp(η^3-allyl)(NO)I], figure 59, the C-C group *trans* to the lower *trans* effect ligand, I, is more tightly held to the metal and is therefore longer at 1.42 Å, but the one trans to NO is 1.37 Å.[273]

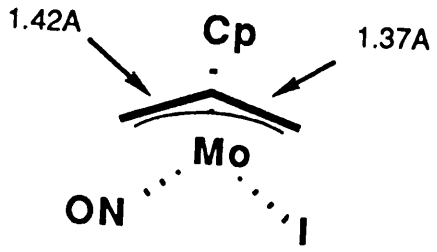
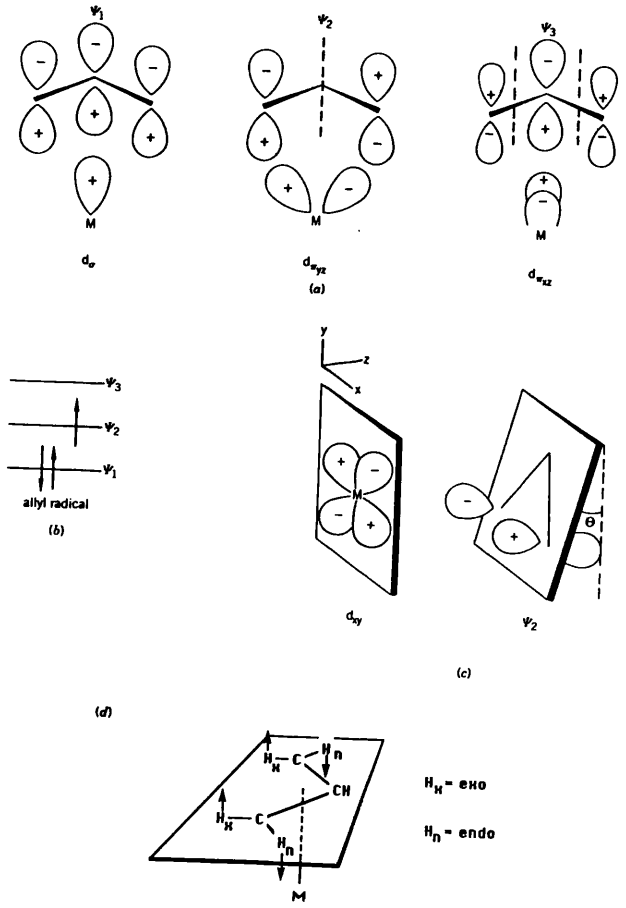


Figure 59 Bond distances in [MoCp(η^3-allyl)NOI]

Figure 60a shows that of the three m.o.'s of the allyl fragment, Ψ_1, can interact with a suitable σ orbital, and Ψ_2 with a d_π orbital on the metal; Ψ_3 is probably of lesser importance.[272] It is also interesting to note that as the number of nodes increases, the m.o.'s of the free ligand becomes less stable (figure 60b).



Nodes are shown as dotted lines

Figure 60 The electronic structure of the allyl ligand and some features of metal-allyl bonding.[272]

Two peculiarities of the structures of η^3-allyl complexes can be understood in this figure. First, the plane of the allyl is canted with respect to the co-ordination polyhedron around the metal, (figure 60c); θ is usually 5-10°. The reason seems to be that the interaction between ψ_2 and the d_{xy} orbital on the metal is improved if the allyl group moves in this way (figure 60c). The second feature of the observed structures is that the terminal CH_2 groups of the allyl are twisted about the C-C vector in such a way as to rotate the exo hydrogens H_x away from the metal, and the endo hydrogens H_n toward the metal, as shown by the arrows in figure 60d. This seems to happen so that the *p*-orbital on these carbons point more directly toward the metal, thus further improving the overlap.[274] The η^3-allyl group often shows exchange of the exo and endo substituents. One mechanism that accomplishes this goes through an η^1-allyl intermediate, as shown in figure 61. This kind of exchange can affect the appearance of the ^{1}H NMR spectrum, and also means that an allyl complex of given stereochemistry may rearrange with time.

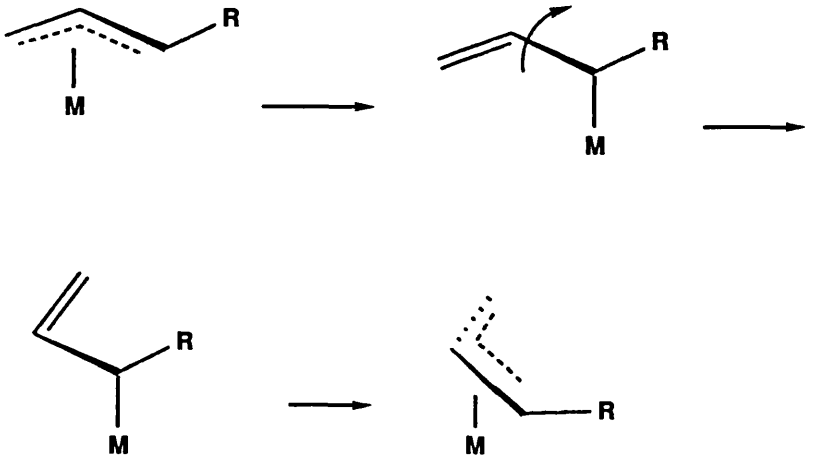
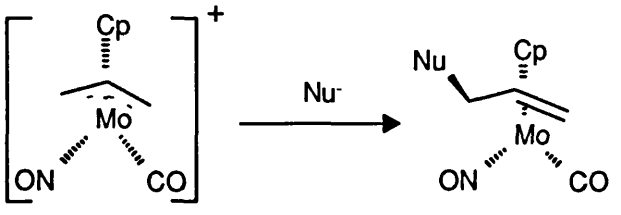


Figure 61 Rearrangements of the η^3-allyl group

C. REACTION OF TRANSITION METAL ALLYLS

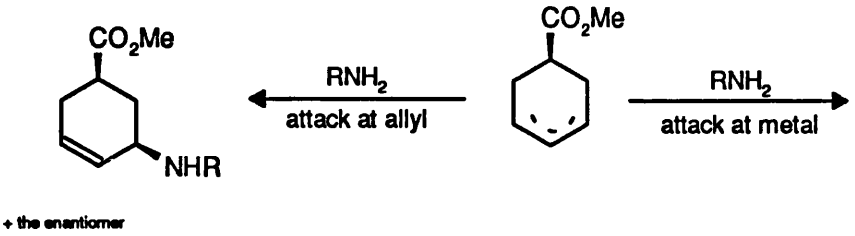
The reactions of transition metal allyls can be divided into four categories:

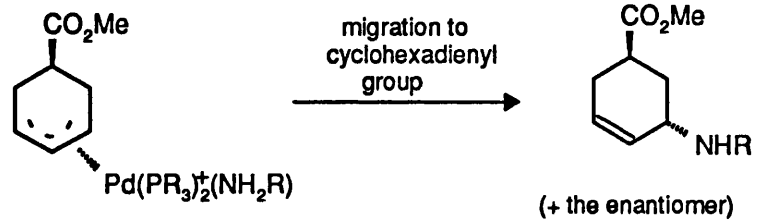
(i) With nucleophiles:[275]



4.7

Nucleophilic attack at one of the terminal carbons of the allyl group most often takes place from the face of the allyl away from the metal. This occurs when the nucleophile attacks directly. Alternatively, cases are known in which the nucleophile first attacks the metal and only then is transferred to the allyl group. The latter route can only take place when a vacant site is made available at the metal. An example of a system that gives products of both stereochemistries is shown below.[276]





4.8

(ii) With electrophiles:[272]

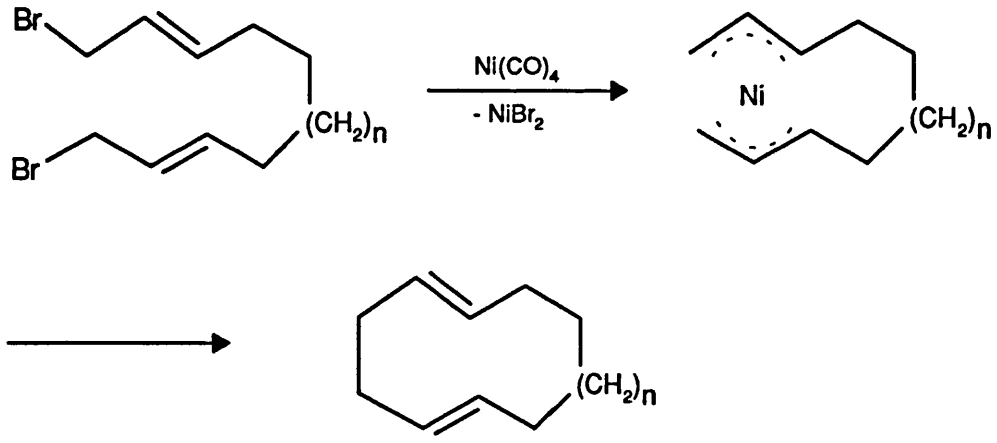
$$[Cp(CO)_2FeCH_2CH{=}CH_2] + E^+ \longrightarrow [Cp(CO)_2Fe(\eta^2\text{-}CH_2{=}CHCH_2E]^+$$

where $E^+ = HgCl^+, Me^+, RCO^+, H^+, Br^+$ **4.9**

(iii) By insertion:[277]

$$[(\eta^3\text{-allyl})_2Ni] \xrightarrow{CO_2} [(\eta^3\text{-allyl})Ni(\eta^2\text{-}O_2CCH_2CH{=}CH_2)]$$ **4.10**

(iv) With reductive elimination:[278]



4.11

4.2.2. TRANSITION METAL CARBONYL COMPOUNDS

A. INTRODUCTION

This section is intended to convey only the briefest overview of the wealth of data encompassing transition metal carbonyl species. More detailed treatises, including many undergraduate textbooks, are widely available.

Metal carbonyl chemistry repeatedly displays two well defined trends; the first is the tendency for the stoichiometries of many, though not all, complexes to adhere to the 18-electron rule (or noble gas formalism). This phenomenon is simply a way of expressing the disposition of the metal atom to use its valence electrons, *nd*, (n+1)*s*, and (n+1)*p*, as fully as possible in forming bonds to ligands. Secondly, in metal carbonyl chemistry, group homology is often, but not always, very pronounced, *e.g.* the similarity of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$.

The choice of preparative scheme employed is determined by the choice of metal atom, though most are synthesised from metal compounds under reductive conditions. The detailed procedures, however, are so enormously varied that the reader is again directed to the earlier reviews.

B. METAL-CARBONYL BONDING

Characteristically in many transition metal carbonyl complexes, the metal atoms exist in low-positive, zero, or negative formal oxidation states. This trait reflects the stabilising influence of the carbonyl ligand. The property is derived from the fact that the ligand, in addition to being a lone pair donor also possess vacant π orbitals. These vacant orbitals are able to accept electron density from filled metal orbitals to form a type of π-bonding that supplements the σ-bonding arising from lone pair donation. The high electron density on the metal atom, of necessity in low oxidation states, is thus delocalised onto the ligands. The manner in which this effect occurs can be described as:

- Overlap of a filled carbon σ-orbital on the metal atom, as in figure 62. The electron flow C→M is offset by pushing electrons back to the vacant orbitals on the ligand.
- A second overlap of a filled $d\pi$ or hybrid $d(p\pi)$ metal orbital with the empty $p\pi$ orbital on the carbon monoxide accepts some of the excess electron density from the metal atom.

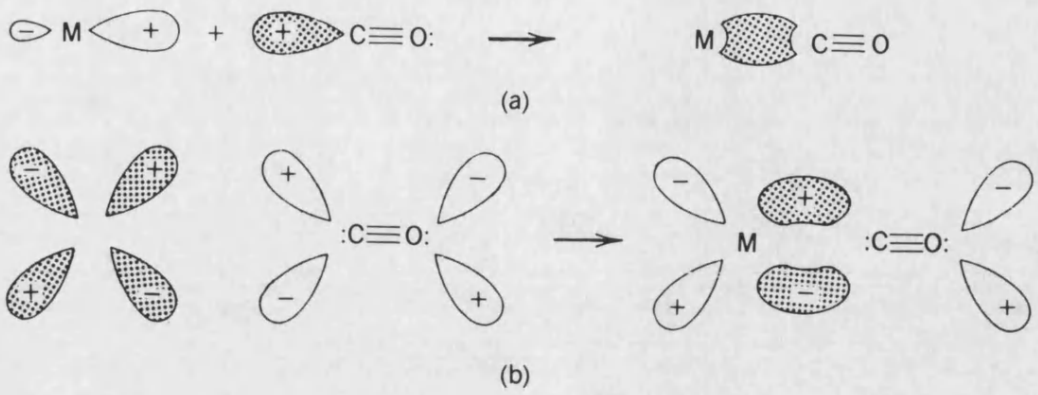


Figure 62 (a) The formation of the metal ← carbon σ-bond using an unshared pair of electrons on the C atom. (b) The formation of the metal → carbon π-bond. The other orbitals on the CO are omitted for clarity.

This transfer of electron denisty from the metal atom to the CO orbitals tends to make the CO as a whole negative and, in turn increases the basicity and, *ergo* electron donation to the metal through the σ-orbital of the carbon. As a result of this drift of electrons, the CO becomes positive and hence enhances the acceptor strength of the π-orbitals. Thus up to a point the effects of σ-bond formation strengthen the π-bonding, and vice versa. This effect is commonly referred to as synergic, or back-bonding.

Experimental evidence from x-ray structural data and vibrational spectra are often used in attempting to understand and rationalise this effect. According to the preceding description of the bonding, as the extent of back-donation from M to CO increases, the M-C bond becomes stronger and the C≡O bond weakens. Thus, multiple bonding is evidenced by shorter M-C and longer C-O bonds compared to M-C single bonds and C≡O triple bonds, respectively. However, x-ray structural studies have shown that in practice only minor variations in bond lengths are encountered, and so interpretation of bonding effects relies primarily on the vibrational spectra of the complexes.

C. VIBRATIONAL SPECTROSCOPY

Although in recent years ^{13}C NMR spectroscopy has become increasingly valuable, infrared (ir) spectroscopy (occasionally in conjunction with Raman spectroscopy) remains the pre-eminent physical method for characterising metal carbonyls.

From the vibrational spectra of metal carbonyls, it is possible to infer the existence and extent of M-C multiple bonding. This is most easily done by studying the CO stretching frequencies rather

than MC stretching frequencies, since the former give rise to strong sharp bands, well separated from all other vibrational modes of the molecule. The inferring of M-C bond orders from the behaviour of C-O vibration depends on the assumption that the valence of C is constant, so that a given increase in the M-C bond order must cause an equal decrease in the C-O bond order; this in turn will cause a drop in the vibrational frequency.

It is also possible to distinguish between terminal and bridging CO groups. For neutral molecules, bridging CO groups absorb in the range 1700 to 1860 cm^{-1} whilst terminal ones generally absorb at higher frequencies (1850-2125 cm^{-1}). However, in using the positions of CO stretching bands to infer the presence of bridging CO groups, it is necessary to keep certain conditions in mind. The frequencies of terminal CO stretches can be quite low if (a) there are a number of ligands present that are good donors but poor π acceptors, or (b) there is a net negative charge on the molecule. In either case, back donation to the CO groups becomes vey extensive, thus increasing M-C bond orders, decreases the C-O bond orders, and so drives the CO stretching frequencies down.

The direct relationship between the symmetry of a molecule and the number of ir active CO also enables the determination of the arrangement of CO groups by comparing the observed spectrum with the number of bands predicted for each of several possible stuctures. In this case it is instructive to study an example, for instance the molecule $[ML_2(CO)_4]$. Figure 63 shows the approximate forms of the CO stretching vibrations and also indicates those that are expected to absorb ir radiation, when only the symmetry of the $M(CO)_4$ portion of the molecule is considered. When L = $(C_2H_5)_3P$, two isomeric compounds can be isolated. One has four ir bands (2016, 1915, 1900, and 1890 cm^{-1}) and is thus the *cis* isomer; the other shows only one strong band (1890 cm^{-1}) and is thus the *trans* isomer.

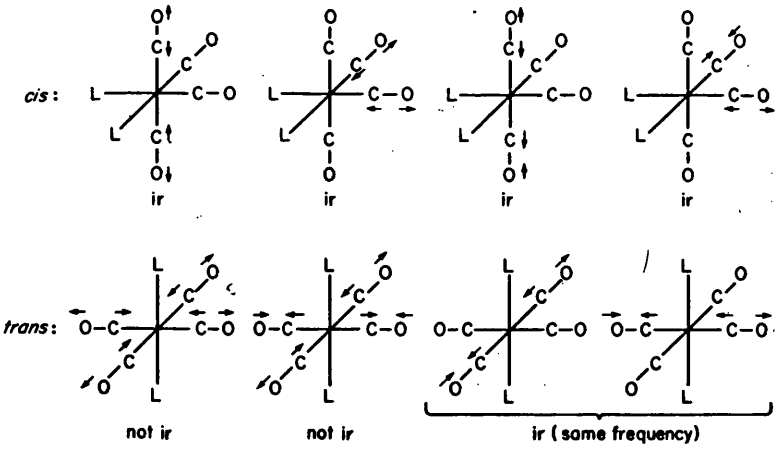
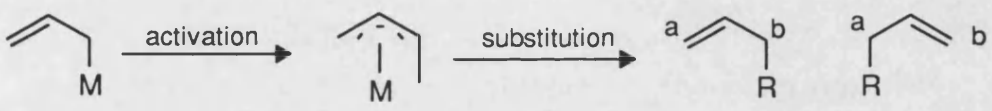


Figure 63 Infra-red active bands in $[Mo(CO)_4(PEt_3)_2]$

4.2.3. CATALYTIC ACTIVITY

A wealth of publications concerning transition metal η^3-allyl complexes exist and, in particular, the synthetic utility and catalytic activity of palladium, molybdenum and nickel complexes have been covered in a number of review papers.[279] Although a comprehensive review of is beyond the scope of this thesis a brief overview is included here.

The well developed chemistry of metal allyl complexes owes much to the discovery of the ability of η^1- and η^3- allyl bonded species to undergo facile conversion to metal co-ordinated alkenes and dienes. Consequently such species find great utility in organic synthesis. Specific interest has centred on the catalysis of allylic alkylations, where the creation of new carbon-carbon bonds has been facilitated by the system's control of the sites available for nucleophilic attack by an incoming substrate.[280] Thus the metallation (activation) step, followed by nucleophilic attack (substitution) results in the formation of a new carbon-carbon bond at either C(a) or C(b). Extensive investigations of these reactions by Trost has revealed that highly regioselective allylic alkylations can be achieved by varying the steric and electronic effects in the η^3-allyl intermediate.[281]



4.12

In low valent transition metals, *i.e.* molybdenum the templating effect of the catalyst is determined by factors such as the degree of metal co-ordination, ligand type and primarily the proximity of the ligands to the allyl group. This is exemplified in $[Mo(\eta^3\text{-}C_3H_5)(acac)(CO)_2(py)]$[282] (figure 64) where the close approach of the ligands to the allyl group ensures that steric control dominates the regioselectivity of the catalyst.

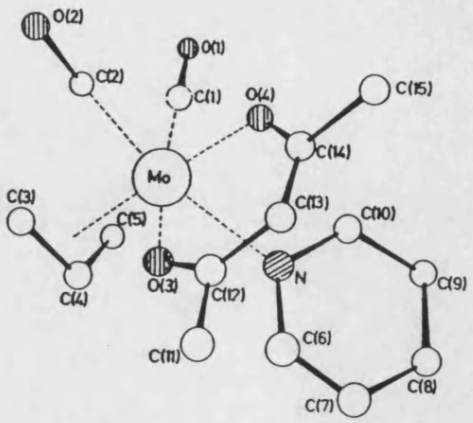


Figure 64 The molecular structure $[Mo(\eta^3\text{-}C_3H_5)(acac)(CO)_2(py)]$

2complex contains two molybdenum(II) allyl dicarbonly chloride units attached to a bridging di-azacrown host *via* Mo-N linkages.

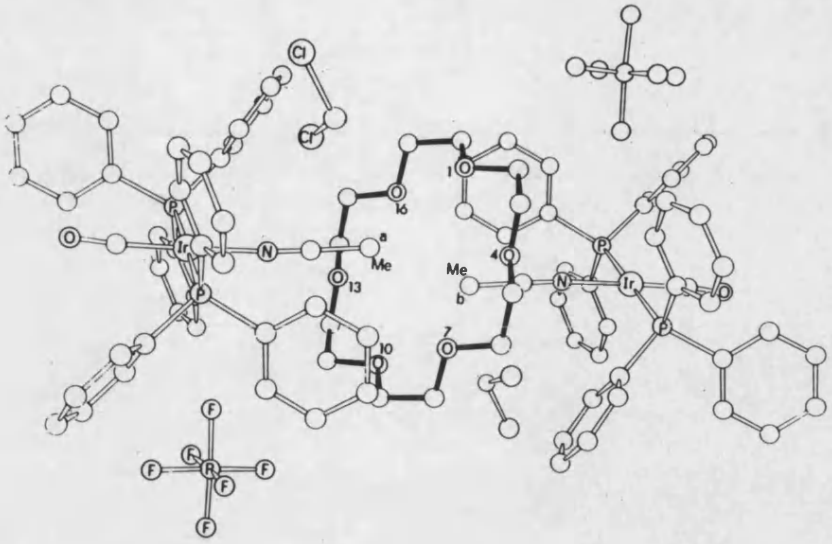


Figure 67 The molecular structure of *trans*-[Ir(CO)(NCMe)(PPh_3)$_2$]PF_6·18-crown-6 (**126**)

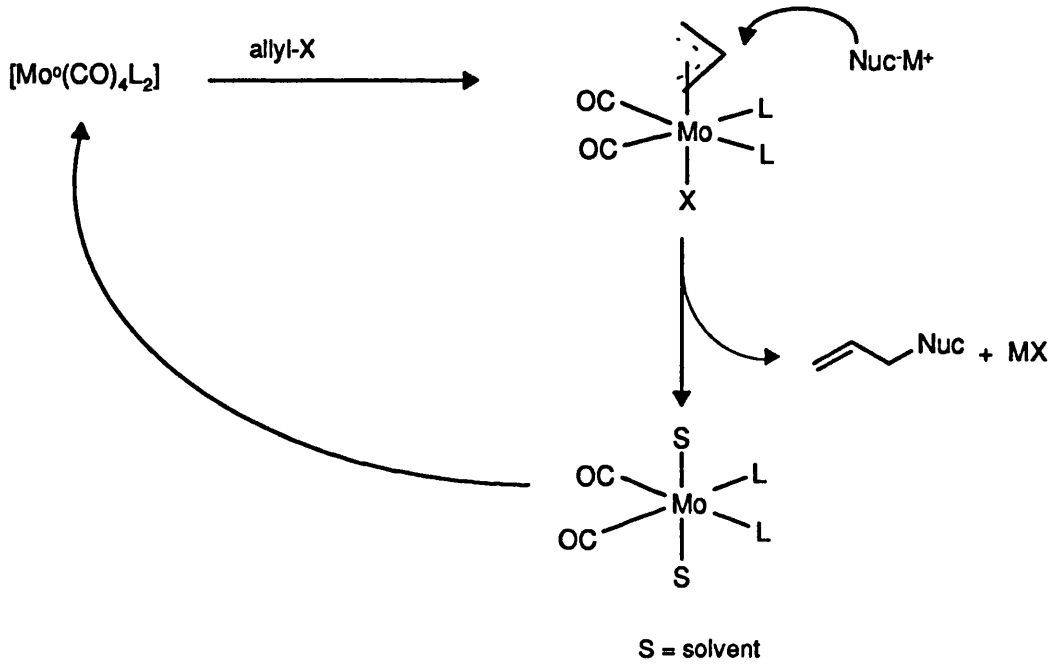
The failure to isolate a well defined, molecular entity was not unsurprsing given Howarths' unsucessful attempts to generate [MoCl(η^3-$C_3H_4CH_2Cl$)(CO)$_2$(L_2)] where L = bipy or dppe from [MoCl(η^3-$C_3H_4CH_2Cl$)(CO)$_2$(NCMe)$_2$].[263] The failure of these displacement reactions has been attributed to the steric bulk of the ligands preventing facile complexation with the metal, and in latter case, a competing reaction involving the allyl group and the basic phosphine. Elimination of an allylphosphonium halide then occurs in generating an unstable molybdenum(0) species. In this study, attempts to overcome similar problems led to two different synthetic approaches being adopted.

In the first case, a one pot synthesis was attempted in conjunction with efforts to replace the chloride ligand with a species that would improve the solubility of the product. Accordingly, a mixture of $Mo(CO)_6$, diazacrown and $CF_3COOC_3H_5$ were refluxed in THF for 6 hours to yield a pale yellow solution. The residue obtained upon removing the reaction solvent was extracted with dichloromethane to afford small colourless crystals of $(CF_3COO)_2^-$·(H_2-diazacrown)$^{2+}$. An analogous reaction using 18-crown-6 failed to realise any solid product after attempts to recrystallise the yellow residue from a variety of solvents.

The second alternative utilises the ability of an isolated [Mo(CO)$_4$L] intermediate, where L = bidentate ligand such as bipy, to undergo oxidative addition reactions with the required allyl species. Thus Howarth succesfully isolated [MoCl(η^3-$C_3H_4CH_2Cl$)(bipy)(CO)$_2$] *via* addition of 3-chloro-2-chloromethylpropene to a [Mo(bipy)(CO)$_4$] intermediate generated from the reaction of $Mo(CO)_6$ with 2,2'-bipyridine.[263] However the reaction of molybdenum hexacarbonyl with an equimolar amount of diazacrown in refluxing toluene afforded a yellow solution from which an insoluble brown

Initial investigations involved the reaction of stoichiometric amounts of the preformed molybdenum (η^3-allyl) catalysts, $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(dppe)]$ where dppe = 1,2-bis(diphenylphosphino)ethane and $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(bipy)]$ where bipy = 2,2'-bipyridine with the anion of 2-carboxmethoxycyclopentanone, and were used to explore the feasibility of the alkylation step. Subsequent testing has employed $[Mo(bpy)(CO)_4]$ and $[Mo(CO)_6]$ as catalysts in the reactions of allylic acetates with the anions of dimethyl malonate and 2-carbomethoxycyclopentanone.

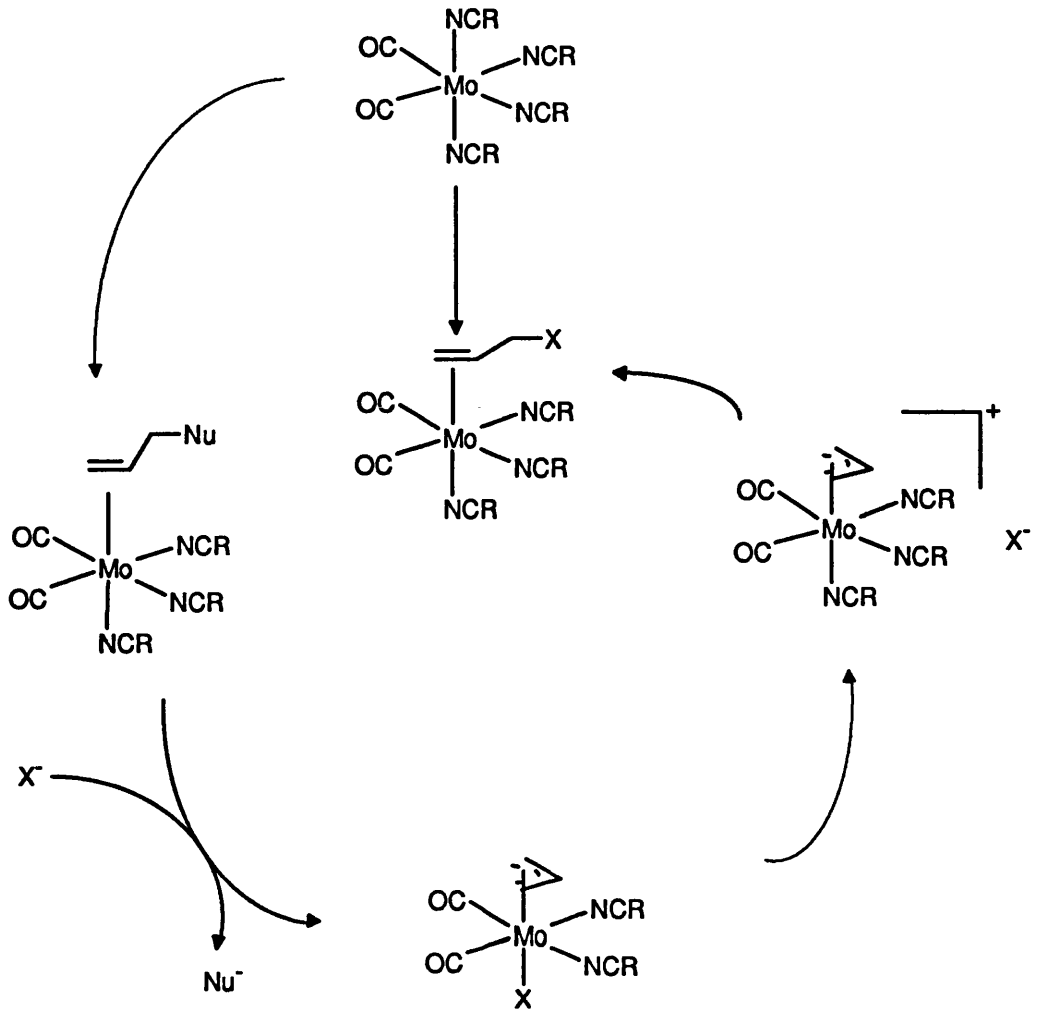
A catalytic cycle (scheme 16) has been proposed in which the intermediacy of a Mo^{II} (η^3-C_3H_5) species is postulated from the limited evidence collected.[280] Thus the reaction proceeds by oxidative addition of the allyl substrate to the molybdenum(0) complex, to form the η^3-allyl complex. Nucleophilic attack on this allylic complex, followed by reductive elimination, gives the allylic substitution product and regenerates the molybdenum catalyst.



Scheme 16 The catalytic cycle of $[Mo(CO)_4L_2]$

However this cycle is hindered by the relatively facile disengagement of carbon monoxide from the ligand, to yield complexes which may no longer function as catalysts. In contrast complexes containing the enhanced σ-donating ability, and lower volatility of isontrile ligands enable the formation of ionised π-allyl complexes which have proved to be extremely important in their reaction with nucleophiles (scheme 17).[280] Hence the complexes $[Mo(bpy)(NCMe)(CO)_3]$ and $[Mo(NCR)_4(CO)_2]$ where R = ^{t}Bu, ^{n}Bu, Ph have proved to be extremely effective catalysts in a wide range of allylic al-

kylations both in terms of reactivity and their ability to exert regioselective control over the attack of the akylating agent.



Scheme 17 The catalytic cycle for $[Mo(NCR)_4(CO)_2]$

RESULTS AND DISCUSSION

4.2.4 CROWN SUPPORTED MOLYBDENUM COMPLEXES

$[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$ (M8), was synthesised using the one-pot preparation reported in 1968 by Hayter.[286]

$$Mo(CO)_6 + C_3H_5Cl \xrightarrow[\text{reflux 16 hrs}]{MeCN} [MoCl(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2] \qquad \textbf{4.13}$$

Thus refluxing molybdenum hexacarbonyl in a mixture of acetonitrile and allyl chloride gave an orange solution which was evaporated to low bulk and then cooled to 0°C. The orange solid (M8) formed in 88% yield did not require further purification and satisfactory elemental analyses were

obtained. Complex (M8) exhibited ν(C≡N) bands in its infrared spectrum centred at 2317 and 2284 cm^{-1}, and two ν(CO) absorptions at 1948 and 1855 cm^{-1} in close agreement to published results,[286] which is consistent with a *pseudo*-octahedral, *cis*-dicarbonyl geometry.

The ^1H NMR spectrum of complex (M8), obtained in CD_3OD, contained a one proton singlet at 3.65 ppm corresponding to the CH of the allyl group. The pairs of *anti* and *syn* protons resonate as doublets at 1.11 and 3.41 ppm, whilst the two methyl cyanide ligands gave a six proton singlet at 2.04 ppm (figure 65). Complex (M8) was found to decompose slowly at room temperature and so was stored under nitrogen at 0°C.

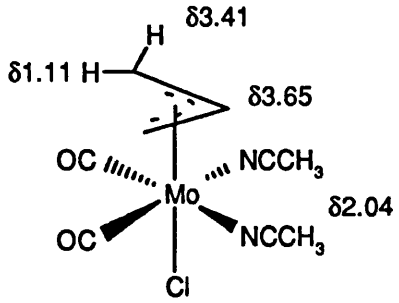
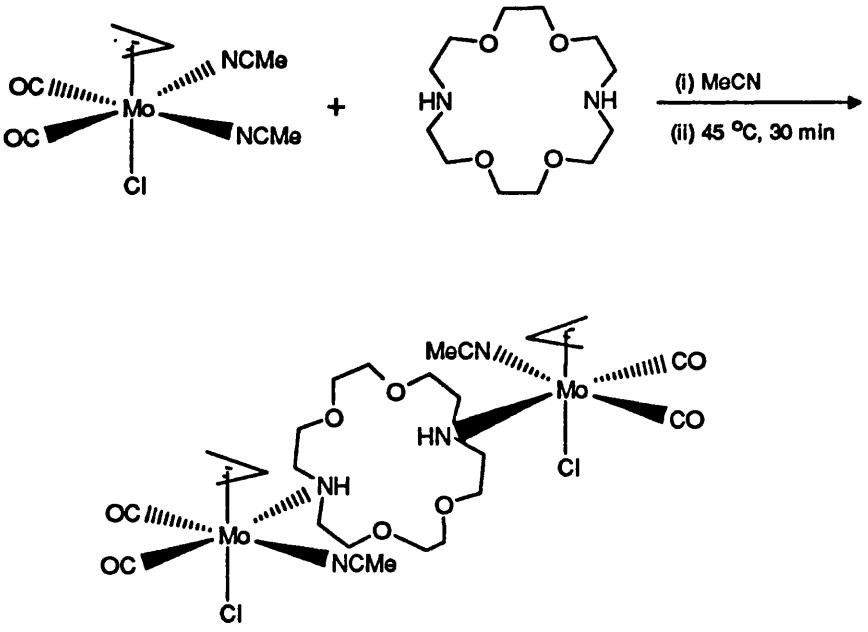


Figure 66 Assignment of ^1H NMR spectrum of $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$ (M8)

In an attempt to assess the ligand displacement reactions of (M8) with aza crown ethers, acetonitrile and THF solutions of the metal complex, warmed (45°C), were treated with 1:1 and 1:2 molar equivalents of monazacrown. A darkening of the solution was observed upon addition of the crown and a solution cell infra-red sample accquired after a reaction time of 1 hour showed shifting of the carbonyl bands to lower wavenumbers (1935, and 1838 cm^{-1}). Removal or reduction in volume of the reaction solvent left a yellow residue which defied attempts to recrystallise it from a variety of common solvents. Efforts to treat the residue with pyridine led to the formation of a dark red, intractable oil from which no solid was recovered.

In contrast addition of an equimolar amount of solid diazacrown to an acetonitrile solution of (M8), warmed to 45°C, immediately generated an insoluble precipitate which was decanted from the liquor to give $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)]_2$·diazacrown (MC1), in 57% yield.



4.14

Complex (**MC1**) was found to be a yellow, reasonably air stable solid, which decomposed slowly on exposure to air. The insolubility of the product in all common solvents prevented further purification but satisfactory elemental analyses were obtained from the crude product.

IR data nujol mull, cm^{-1}	ν(C≡O) 1919, 1821, ν(N-H) 3231, ν(C-O) 1132
Microanalysis (Calc for $C_{26}H_{42}Cl_2N_4O_8Mo_2$)	C 38.9 (38.9), H 5.18 (5.37), N 6.86 (7.14)

Table 44 Selected analytical data for $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)]_2$·(diazacrown)

Two vibrational bands centred at 1919 and 1821 cm^{-1} are assigned to ν(C≡O) modes in agreement with an expected *cis*-dicarbonyl geometry. Weak absorptions at ν(N-H) 3231 and, ν(C-O) 1132 cm^{-1} are indicative of the diazacrown macrocycle, whilst the presence of acetonitrile was inferred through a band, due to ν(C≡N) centred at 2362 cm^{-1}. Repeatedly washing the product with diethyl ether or acetone resulted in the bright green colour of the solid fading to a darker green, and a concomitant decrease in the relative intensity of the ν(C≡N) band. This is suggestive of a complex in which the acetonitrile is retained within the co-ordination sphere of the molybdenum atom (reaction 4.14). Further studies (including NMR spectroscopy) of (**MC1**) were prevented by the insolubility of the product.

Host guest complexes involving two metal guests to a single oxa-macrocycle have been observed previously in neutral, and cationic iridium (**126**) and platinum (**127**) complexes of 18-crown-6 (figure 67). A similar arrangement can therefore be envisaged for (**MC1**) in which the nitrogen donors of diazacrown displace a single acetonitrile ligand from two molecules of (**M8**), the resultant

solid $[Mo_2(CO)_6(diazacrown)]$ (**MC2**) was recovered in 57% yield. The air sensitive compound displayed no significant solubility in any common solvent except dimethylsulfoxide.

$$Mo(CO)_6 + \text{diazacrown} \xrightarrow[\text{2hr reflux}]{\text{Toluene}} [Mo_2(CO)_6(\text{diazacrown})] \qquad \textbf{4.15}$$

Microanalysis was in good agreement with the formulated product. The IR spectrum of (**MC2**) exhibited strong ν(C≡O) bands at 1908, 1790 and 1736 cm^{-1}, consistent with a neutral molybdenum tricarbonyl grouping.[283] Absorptions due to the diazacrown were observed at 3322 and 3273 cm^{-1}, ν(N-H) and ν(C-O) at 1129 cm^{-1}. Both ^1H and $^{13}C\{^1H\}$ data show the presence of only a single crown environment but no carbonyl resonances were observed. The latter effect is attributed to the relative rapid decomposition of the product in solution compared to the time taken to acquire the $^{13}C\{^1H\}$ NMR spectrum

IR data, nujol mull, cm^{-1}	ν(N-H) 3322 and 3273, ν(C≡O) 1908, 1790 and 1736, ν(C-O) 1129
Microanalysis (Calc for $C_{18}H_{24}N_2O_{10}Mo_2$)	C 34.7 (34.8), H 4.60 (4.22), N 4.83 (4.61)
^1H NMR, δ(ppm) (d_6-DMSO)	3.04 (8H, br s, CH_2NHCH_2), 3.65 (8H, br s, OCH_2CH_2O), 3.92 (8H, br s, OCH_2CH_2O)
$^{13}C\{^1H\}$ NMR, δ(ppm) (d_6-DMSO)	47.9 (CH_2NHCH_2), 67.7, 69.4 ($CH_2CH_2OCH_2CH_2$)

Table 45 Selected analytical and spectroscopic data for $[Mo_2(CO)_6$·(diazacrown)] (**MC2**)

It is well established that heating at high temperatures a mixture of $[Mo(CO)_6]$ and bidentate ligands containing an acidic hydrogen atom can result in oxidative decarbonylation, giving multiple metal-metal bonded compounds when only one non-hydrogen atom is bonded to the two ligating atoms of the ligand.[284a] The exact nature of the metal entity to which the crown is bound in (**MC2**) remains uncertain, with both a Mo-Mo multiply bonded, $[Mo_2(CO)_6]$ unit or two independent $Mo(CO)_3$ fragments being possible. Mass spectrometry was used in an attempt to clarify the nature of the $[Mo(CO)_3]_n$ unit, but no identifiable molecular ion or fragmentation pattern could be detected.

In order to investigate this effect further, analogous reactions with $Cr(CO)_6$ and $W(CO)_6$ were undertaken. In the former, a solid was obtained from a refluxed solution of toluene containing equimolar amounts of $Cr(CO)_6$ and diazacrown. Sublimation of the product removed unreacted $Cr(CO)_6$ to afford an orange solid which was found to be air sensitive but soluble in common polar organic solvents. Examination of the vibrational spectrum of (**MC3**) showed the presence of two strong bands at 1977 and 1908 cm^{-1} consistent with the ν(C≡O) stretching modes of a dicarbonyl chromium complex. Additional absorptions due to the diazacrown were observed at, 3335 cm^{-1}, ν(NH), and at

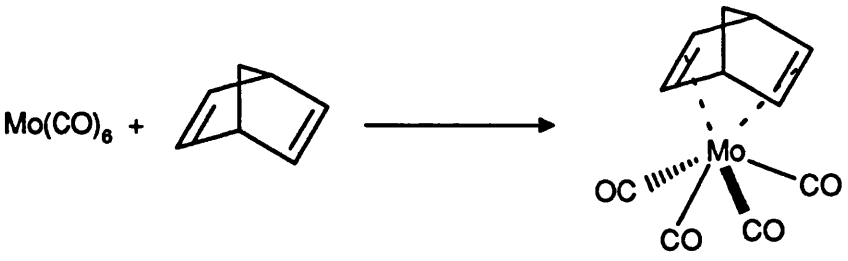
1129 cm^{-1}, ν(C-O). Although the ^1H and $^{13}C\{^1H\}$ NMR data indicated the presence of only a single diazacrown moiety, elemental analysis exhibited lower than expected values for carbon, hydrogen and nitrogen (table 46).

IR data, nujol mull, cm^{-1}	ν(CO) 1977, 1908; ν(NH) 3335; ν(C-O) 1154
Microanalysis (Calc for $C_{14}H_{25}N_2O_6Cr$)	C 52.1 (45.4), H 8.70 (7.09), N 8.27 (7.61)
^1H NMR, δ(ppm) ($CDCl_3$)	2.82 (8H, br s, CH_2NHCH_2), 3.63 (16H, br s, $CH_2CH_2OCH_2CH_2$)
^{13}C NMR, δ(ppm) ($CDCl_3$)	49.5 (CH_2NHCH_2), 70.4 ($CH_2CH_2OCH_2CH_2$)

Table 46 Selected analytical data for complex (MC3)

Additional attempts to purify (MC3) *via* recrystallisation from a variety of common organic solvents resulted in the decomposition of the product. Reaction of $W(CO)_6$ with diazacrown in refluxing toluene for up 12 hours afforded yellow solutions from which unreacted $W(CO)_6$ was recovered and a moderately air sensitive yellow residue. The latter defied all attempts to purify it by recrystallisation or column chromatography, producing only intractable oils containing no carbonyl groups.

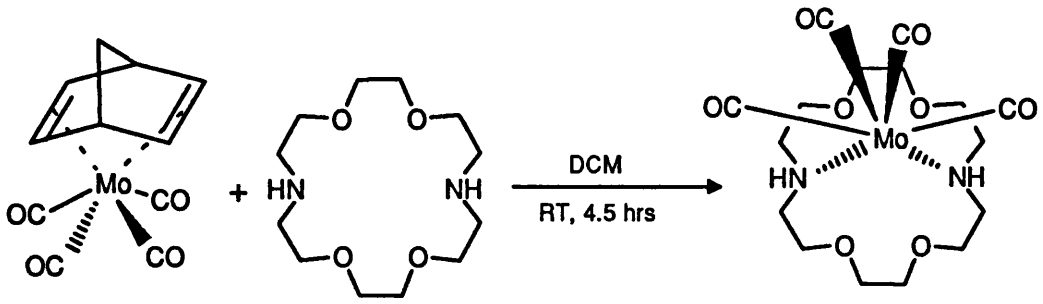
An alternative strategy involved the replacement of a weakly co-ordinating ligand, such as cyclooctadiene. Thus $[Mo(C_7H_8)(CO)_4]$ was prepared according to the literature method detailed by King which involved refluxing a mixture of molybdenum hexacarbonyl and bicycloheptadiene in methylcyclohexane for 16 hours. Cooling the resulting suspension to room temperature, and filtering under nitrogen, through glass wool stood over a frit gave a clear filtrate which was reduced to low bulk under vacuum. The brown residue obtained after storing at -30°C overnight was then sublimed *in vacuo* to yield the pure material in 14% yield.



4.16

Micronalysis of the product was in good agreement with the expected values and confirmed that no further purification was required. Examination of the infra-red spectrum showed ν(C≡O) stretching bands at 2030, 1980-1920 and 1870 cm^{-1} consistent with a neutral tetracarbonyl complex, and in good agreement with reported values.[287]

Addition of a dichloromethane solution of diazacrown to (M9) readily displaced the bicycloheptadiene ligand to yield *cis*-[Mo(CO)$_4$(diazacrown)] (MC4) as a yellow solid in 93% yield.



4.17

Complex (MC4) was found to be soluble in a variety of solvents and, stable under nitrogen but rapidly decomposed on exposure to air to yield a brown solid containing no carbonyls. Satisfactory elemental analyses were obtained, and the infra-red spectrum exhibited four carbonyl bands at 2008, 1879, 1852, and 1802 cm^{-1} within the range previously reported for [Mo(CO)$_4$(L)$_2$] complexes.[284] The bands of medium, very strong, strong as a shoulder, and strong intensity by decreasing frequencies are as expected for a *cis*-[M(CO)$_4$(L)$_2$] complex, where M represents a transition metal atom and L_2 is one bidentate ot two monodentate ligands. A ν(NH) absorption due to the crown was observed at 3216 cm^{-1} which falls within the range of values reported for ligands co-ordinated to a molybdenum centre through an HN···Mo linkage.[284a] The ^{1}H and ^{13}C{^{1}H} NMR spectra showed only a single crown environment but no carbonyl absorptions.

IR data, nujol mull, cm^{-1}	ν(C≡O) 2008, 1879, 1852, 1802; ν(NH) 3216; ν(C-O) 1119
Microanalysis (Calc for $C_{16}H_{26}N_2O_8Mo$)	C 40.6 (40.8), H 5.80 (5.58), N 5.82 (5.99)
^{1}H NMR (CD_2Cl_2)	2.86 (t, 8H, CH_2NHCH_2), 3.66 (s, 16H, OCH_2CH_2O)
^{13}C{^{1}H} NMR (CD_2Cl_2)	49.8 (CH_2NHCH_2), 70.6 (OCH_2CH_2O)

Table 47 Selected analytical data for [Mo(CO)$_4$(diazacrown)] (MC4)

The failure to isolate a soluble, discrete molecular product using diazacrown as a supporting macrocycle led to attempts to displace both nitrile and chloride ligands from (M8) using a triazacrown moiety (reaction 4.18).

$$[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2] + \text{1,4,7-triazacyclononane} \xrightarrow[NH_4PF_6 \text{ or } KPF_6]{MeCN} [Mo(\eta^3\text{-}C_3H_5)(CO)_2(\text{1,4,7-triazacyclononane})]PF_6 \qquad 4.18$$

Thus studies by Davies[288] and subsequently Harwood[280] found that the one pot reaction of (M8) with triazacyclononane and NH_4PF_6 in acetonitrile leads to the formation of $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(1,4,7\text{-triazacyclononane})]PF_6$ (MC5).

IR nujol mull, cm^{-1}	ν(N-H) 3427 and 3327, ν(CO) 1933 and 1850
Microanalysis (Calc for $C_{11}H_{20}F_6MoN_3P$)	C 26.5 (26.3), H 4.15 (3.98), N 8.43 (8.36)
^1H NMR (CD_3CN)	1.14 (2H, d, $CH_aH_sCHCH_aH_s$), 2.65 (2H, d, crown), 3.14 (10H, s, crown), 3.15 (2H, d, $CH_aH_sCHCH_aH_s$), 3.61 (1H, sept, $CH_aH_sCHCH_aH_s$)
$^{13}C\{^1H\}$ NMR (CD_3CN)	48.7 (CH_2CHCH_2), 54.0 (crown), 70.5 (CH_2CHCH_2), 206.3 (CO), 238.4 (CO)

Table 48 Selected analytical data for $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(1,4,7\text{-triazacyclononane})]PF_6$

The air stable product was found to be soluble in polar organic solvents, and crystals suitable for a x-ray structural determination were isolated upon recrystallisation from an acetone/diethyl ether solution (figure 68). Structural analyses of the cationic molybdenum moiety and its disordered counterion as well as attempts to refine the synthetic procedure are discussed elsewhere.[280, 288]

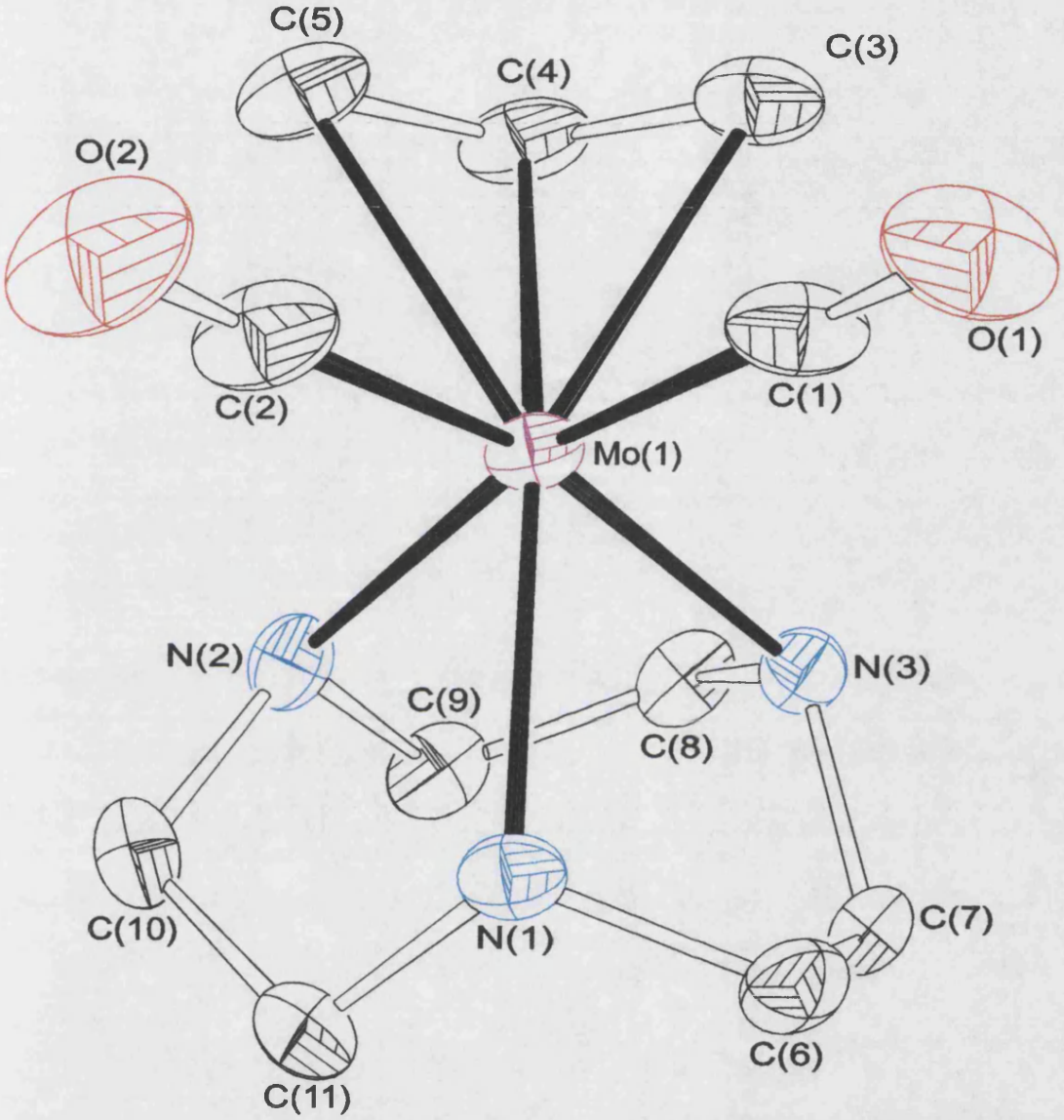


Figure 68 Molecular structure of the cation $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(1,4,7\text{-triazacyclononane})]^+$

Chapter Five: Conclusions and Recommendations

5.1 CONCLUSIONS

The adsorption of a catalytically active metal moiety onto the surface of a supporting substrate to yield a heterogeneous catalyst can often result in tangible changes to the reactivity and selectivity of the appended metal centre. In attempts to probe these effects, the active metal entity can be attached to ligand sets which are regarded as paradigms of the normal support. For the first set of potential model supports considered within this study; silanols and siloxanes their effect upon the metal centre has been addressed through the synthesis and structural characterisation of isolable molecular species. Similarly the modes of oxa- and aza- crown ether bonding to low oxidation state molybdenum moieties were investigated in an attempt to elucidate the catalytic cycles and activity of molybdenum(allyl)dicarbonyl species.

In addition, solid-state and solution studies of silanol-crown interactions have been undertaken, the results of which may provide information on the type of interactions occurring in water-sediment interfaces. The information obtained may also be of use in assessing the viability of silanols as sequestering agents for the extraction of toxic organic residues, particularly crown-ethers, from aqueous solvent mixtures.

5.1.1 MOLYBDENUM AND TUNGSTEN SILOXIDES AND SILOXANES

In the case of processes in which a reactive moiety is tethered to a silica support, attachment generally occurs *via* a linkage to surface hydroxyl sites. It is argued that reactivity of the metal species is moderated at the silica-metal interface by the number and type of hydroxyl functions to which it binds. In order to examine this relationship several model silanols containing differing organic functionalities, numbers of potential binding sites and spacings were prepared in the early part of this investigation. They included tetramethyl-1,3-dihydroxydisiloxane, and its disodium salt, tetraphenyl-1,3-dihydroxydisiloxane, di-*tert*-butyl-1,1,3,3-tetrahydroxydisiloxane, heptacyclohexyl-heptasiloxane-1,6,7-triol and sodium triphenylsilanolate.

Efforts to mimic single, isolated hydroxyl sites using a monodentate siloxide ligand, resulted in the successful synthesis of a number of oxo- and dioxo-tungsten triphenylsiloxide complexes. The reaction of $[W(O)Cl_4]$ and $[W(O)_2Cl_2(L)_2]$ where L = DMSO, TMSO and Ph_3PO with Ph_3SiONa gave the compounds $[W(O)Cl(OSiPh_3)_3]$ and $[W(O)_2(OSiPh_3)_2(TMSO)_2]$ which displayed the anticipated terminal geometry of bulky siloxide ligands. In the former reaction, addition of Ph_3SiONa to

$[W(O)Cl_4]$ appears to be independent of stoichiometric control. The reasons for the incomplete substitution of the chloride ligands cannot be solely attributed to the steric bulk of the triphenylsiloxide ligand (complete replacement has been reported with sterically bulkier alkoxides), but may also be affected by the synthetic route utilised. An unusual bridging mode appears to be adopted by the triphenylsiloxide ligand in the aggregation of two five co-ordinate tungsten centres in $[W(O)_2(\mu\text{-}OSiPh_3)L]_2$, where L = DMSO and Ph_3PO. The formation of an insoluble white solid upon the addition of potassium trimethysilanolate to the tungsten(oxo) chlorides confirmed the propensity of these species to form bridged tungsten species.

The consequences of binding a metal centre to two hydroxyl sites on silica were modelled by the reactions of $[W(O)Cl_4]$ with $Ph_2Si(ONa)_2$ and $[Ph_2Si(ONa)]_2O$ respectively. The metallasiloxane, $[WO\{OSiPh_2O\}_2]_4$, which represents a geminal interfacial site was spectroscopically characterised but attempts to mimic vicinal hydroxyl sites by coupling the metal centre to tetraphenyl-1,3-dihydroxydisloxane failed.

The spectroscopic evidence for the structures of these compounds could not be confirmed by crystallographic data so uncertainties regarding the structural detail and electronic effects of bonded siloxide and siloxane ligands remain. In order to extend this work, structural data should be sought on analogues despite the sensitivity of the compounds to air and moisture. Additional π-donor ligands such as phosphines or amines may be employed in efforts to stablise the metal centre, however the presence of these competitive π-donors may in turn moderate the effects of the siloxide ligand.

In deliberating the use of metal-halide elimination reactions as a route for the preparation of molybdenum, and especially tungsten, siloxides an inspection of the literature clearly reveals that the synthesis of analogous alkoxide species has been beset by similar problems to those found in this study; *i.e* the susceptibility of the reactants to moisture, and the inclusion of solvents and by-products into the complexes. These difficulties render metal-halide elimination reactions synthetically unattractive and thus future work should include a rigorous assessment of the alternative synthetic strategies available. Due consideration should be given to methodolgies employed in the successful isolation of molybdenum and tungsten alkoxides.

As an alternative to metal-halide metathesis reactions, the use of the oxophilic nature of the metal centre to abstract oxygen from a variety of reagents was pursued to some degree in this study. Some advantages of oxygen abstraction processes are illustrated by the generation of $[W(O)Cl_4]$, and $[W(O)_2Cl_2]$ by the addition DCM or octane solutions of hexamethydisiloxane to WCl_6 and $[W(O)Cl_4]$ respectively. It has been shown that DCM and acetonitrile solutions of hexaphenylcyclotrisiloxane react with WCl_6 in an analogous manner to produce tungstenoxy chloride from the metal hexachloride. Repeating this reaction in THF resulted in a viscid blue oil which upon oxidation af-

forded a sticky white solid which analysis showed to be an unknown molecular weight ring opened THF polymer. Although WCl_6 and $[W(O)Cl_4]$ are recognised as ring-opening catalysts neither has been previously reported to polymerise THF, and it is postulated that the reaction chemistry is determined by the formation of an unstable tungstasiloxane intermediate.

An air stable spirocyclic oxo tungsten siloxane $[WO\{O(Ph_2SiO)_3\}_2 \cdot THF]$ was isolated in low yield upon reaction of $[W(O)Cl_4]$ with $[Ph_2SiO]_3$ in THF. A structural determination of the complex revealed Si-O-W bond lengths [W-O(Si)$_{av}$ 1.879 Å] to be consistent with significant $O(p\pi) \rightarrow M(d\pi)$ donation. The potential mechanisms leading to the formation of the oxo tungstensiloxane are discussed in terms of the stabilising influence of the solvent and the ring strain within the cyclic siloxane. Whilst the attractiveness of employing cyclosiloxanes to produce metallasiloxanes is diminished by the low yield obtained, the potential to generate novel complexes should ensure continued work. For this reason the reactions of other oxophilic metal centres with strained cyclotri-, or even cyclodi-siloxanes should be pivotal to further studies.

In contrast to the less reactive molybdenum species binuclear tungsten alkoxide, and especially siloxide, complexes containing metal-metal bonds have been noted to act as models for Fischer-Tropsch process as well as being highly effective polymerisation catalysts. These compounds are attractive as the metal atoms behave as Lewis acid centres with the presence of M-M bonds providing a reservoir of electrons for π-acid susbtrates. To-date alkoxide and siloxide complexes containing metal-metal (M = Mo, W) single, double and triple bonds have been characterised and their reactivity investigated, but no complexes with a M-M quadruple bond are recorded. Attempts to couple triphenylsilanol, diphenylsilanediol and sodium tetramethyldisiloxane diolate to either $[Mo_2(O_2CCH_3)_4]$ or $K_4[Mo_2Cl_8]$ whilst preserving the M-M bonds were largely unsuccessful. In the first case the dimolybdenum carboxylate proved to be too insoluble and unreactive, and as a result was recovered unchanged from the reaction mixtures. In the latter case, $K_4[Mo_2Cl_8]$ appeared to have undergone limited ligand substitution, but the products were too insoluble to separate and identify. Additional work using silanols and more reactive metal complexes might be profitable and yield species of catalytic interest.

5.1.2 CROWN ETHER-SILANOL COMPLEXES

The hydrogen-bonding properties of silanols has been exploited in the study of siliceous materials at the sedimentary-water interface, and silanols have also been used to selectively abstract organic residues from mixtures of aqueous organic solvents. Despite the large number of silanol species structurally characterised there is a paucity of literature information concerning simple adduct formation of relevance to the above.

Hydrogen-bonding interactions have been observed previously by single crystal X-ray diffraction studies of $(Ph_3SiOH)_2$·12-crown-4. The use of oxa- and aza- crown ethers in this study has enabled the binding preferences of the silanol ligand towards the N or O donors of the crown, and consequently how this effects the maximum number of co-ordinated guests to be examined.

Triphenylsilanol reacts in hot toluene solutions of oxo- and diaza- crown ethers to generate the binary complexes $(Ph_3SiOH)_3$·18-crown-6 and $(Ph_3SiOH)_2$·diazacrown respectively. Spectroscopic characterisation of the compounds indicates that the latter forms Si-OH···NH links which are stronger than the Si-OH···O hydrogen bonds in the former. It is recommended that further studies should include structural determinations on both these compounds.

The high affinity of 18-crown-6 for water was demonstrated by the hygroscopic nature of $(Ph_3SiOH)_3$·18-crown-6 and its decomposition in solution to yield $(Ph_3SiOH)_2$·18-crown-6·$(H_2O)_2$. A structural determination of the ternary complex revealed that both triphenylsilanol ligands bind to the crown *via* co-ordination to intermediate water molecules. Similar effects were revealed by a structural investigation of $(Ph_3SiOH)_2$·monoazacrown·(H_2O) in which one silanol ligand is co-ordinated to the crown *via* an intermediate water molecule whereas the other links to the crown by a direct Si-OH····NH interaction.

^{29}Si NMR spectroscopy revealed that the 18-crown-6 adducts readily dissociate in solution to give the free crown ether and triphenylsilanol, whilst the stronger Si-OH···NH interactions present in the monoaza- and diaza- crown ether - silanol complexes ensure that the former remains partially, and the latter completely, intact in solution. The greater strength of the Si-OH···NH interaction in comparison to the Si-OH···O interaction can be attributed to the ability of the nitrogen atom to function as a superior proton acceptor.

Preliminary studies on the interaction of crowns with bidentate silanols failed to yield discrete molecular entities. IR data, microanalysis and ^{1}H NMR studies indicated that complex mixtures of products were formed in which cyclisation of the silanol may occur. Further work should include an assessment of the silicon containing products present in such solutions using ^{29}Si NMR techniques.

5.1.3 TRANSITION METAL- OXA- AND AZA- CROWN COMPLEXES

Many transition metal η^3-allyl species have been successfully prepared by the oxidative addition of the catalytically active $[M(CO)_4(L)_2]$ and $[M(CO)_3(L)_3]$ complexes, where M = Mo, W and L = monodenate or bidentate ligand. Thus refluxing toluene and THF solutions of $M(CO)_6$ (M = Cr, Mo, W) were reacted with 18-crown-6, monoazacrown, and diazacrown in an attempt to isolate the disubstituted metal(0) tetracarbonyl intermediates. The oxa- and monoaza- crown ethers failed to

generate an isolable molybdenum carbonyl complexes but [$Mo_2(CO)_6$·diazacrown] was formed. The insolubility of the complex prevented its complete characterisation as either a metal-metal bonded [$Mo_2(CO)_6$] containing species or as a complex with two independent [$Mo(CO)_3$] fragments. It is therefore recommended that future work should continue in this area in which Raman spectroscopy could provide valuable information on the possible existence of a metal-metal bond. Analogous reactions with chromium and tungsten hexacarbonyl failed to produce clearly defined products, however vibrational spectroscopy indicated that a chromium dicarbonyl species may have been formed. An alternative approach to producing [$Mo(CO)_4(L)_2$] species involves the displacement of a weakly co-ordinated ligand *via* a stronger donor ligand. Thus addition of a dichloromethane solution of diazacrown to [$Mo(CO)_4(C_7H_8)$] readily led to the replacement of bicycloheptadiene, and accordingly [$Mo(CO)_4$·(diazacrown)] was isolated towards the end of the work. It is anticipated that additional studies should yield isolable diazacrown supported metal carbonyl species which may permit entry into Mo(II) allyl derivatives *via* oxidative addition routes.

Transition metal η^3-allyl complexes find widespread use in synthetic organic chemistry. In these laboratories as well as elsewhere, interest has centred on molybdenum(allyl)dicarbonyl reagents which act as highly regioselective catalysts for the creation of new carbon-carbon bonds. The complex nature of homogeneous processes often results in many species being involved in the catalytic cycle but of particular importance in alkyne oligomerisation is believed to be the cationic species $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_3]^+$. In this study an attempt was made to prepare analogues using macrocycle donors.

Initial attempts to stabilise the molybdenum(allyl)dicarbonyl unit using oxa- and aza- crown compounds highlighted the propensity of the metal entity to form stable complexes only with compounds containing the "softer" nitrogen donor atoms. Thus $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)]_2$·(diazacrown) and $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(\text{triazacrown})]^+PF_6^-$ were readily prepared by ligand displacement reactions from the metal complex $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$. The latter complex was also characterised by single crystal x-ray diffraction. Attempts to produce 18-crown-6 and 1-aza-18-crown-6 analogues by either a displacement reaction from $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$ or *via* a one pot synthesis were unsucessful.

5.2 RECOMMENDATIONS FOR FURTHER WORK

5.2.1 MOLYBDENUM AND TUNGSTEN SILOXIDES AND SILOXANES

The primary objectives and advantages in studying metal entities attached to model substrates lie in the quantative bond data obtained from crystallographic studies, the ability to test the catalytic ac-

tivity, and study spectroscopically the reactions of isolated molecular species. Consequently additional work should emphasise extending the range of model complexes containing molybdenum and tungsten, oxo- and dioxo- species, which have widespread importance as both oxo-transfer and polymerisation catalysts. By also expanding the range of model substrates to include all possible interfacial geometries our understanding of the role of silica surfaces in determining the reactivity of the metal centre will be greatly enhanced. The following tasks represent the most pertinent points for prospective studies:

1. Single crystal X-ray diffraction studies: Without the detailed bond data acquired in crystallographic studies an understanding of the effects of the siloxide ligand on the metal centre remain at best qualitative. A comparison of bond lengths and angles, and hence their implied O($p\pi$)→M($d\pi$) effects, may further help elucidate the differences in reactivity witnessed initially in Chisholm's and Wolczanski's studies of early transition metal (Zr, Ti and Ta) alkoxides and siloxides, and later in their mechanistic studies of the metal-metal bonded molybdenum and tungsten complexes.

2. Appraisal of synthetic methodology: The paucity of structural information relating to tungsten siloxides is a reflection not only on the difficulty in handling tungsten precursors, but in the methodologies employed in their synthesis. Metal halide metathesis reactions suffer not only from the sensitivity of the reagents to moisture but also the difficulty in separating the products from impurities. This approach may also be hindered by the highly oxophilic nature of the tungsten metal causing heterolysis of the Si-O bond in order to produce extremely stable tungsten oxides. Consequently alternative synthetic strategies should be employed;

   The most successful general synthetic strategy in producing high oxidation state tungsten moieties has been the direct metathesis between a silanol and a less acidic alkyl or amide. The greater solubility of the organotungsten reagents obviates the need for co-ordinating solvents and the products can be easily separated from the side products which are usually gases or volatile liquids. The problems of extreme moisture sensitivity and susceptibility to Si-O-M bond heterolysis remain a considerable difficulty with this methodology.

3. Further investigation of the ring opening reactions of strained siloxanes: As previously discussed, oxophilic metal centres have been shown to react with cyclosiloxanes to yield both linear and cyclic metallasiloxanes. The studies indicate that the successful outcome of the reactions is dependent upon the degree of ring strain inherent in the ring system, accordingly in addition to hexaphenylcyclosiloxane, potential substrates for study could include Fehers cage complex [$Cy_6Si_6O_9$], and the smaller borasiloxanes

4. Addition of crown ethers to the ring opening reactions of tungsten oxo chloride and strained cyclosiloxanes: Ring opening reactions have been found to proceed more efficently in the presence of a stabilising solvent such as THF. Crown ethers also function as highly effective stabilising agents in reactions involving charged or polar intermediates. Thus a comprehensive evaluation of the presence of such compounds in high oxidation state transition metal mediated ring opening of cyclosiloxanes may realise metallasiloxanes in higher yield.

5. Evaluating a wider range of metal co-ordination environments: Additional work may focus on refining the steric and electronic impact of the model substrate on the metal centre by selecting silanols containing the appropriate substituents on the silanol. To-date $[Me_2Si(OH)]_2O$, $[Ph_2Si(OH)]_2O$, $[^tBuSi(OH)_2]_2O$, and the trisilanol $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3]$ have been prepared in synthetically useful quantaties. Utilisation of these materials in conjunction with the commercially available Ph_3SiOH, and $Ph_2Si(OH)_2$ or by appending the metal entity to one of the more esoteric silanols described in the introductory chapter would elucidate the consequences of tethering a transition metal centre to a wide range of anticipated interfacial environments.

6. Investigating the use of tungstasiloxanes as polymerisation catalysts: This study reports that the addition of $[Ph_2SiO]_3$ in THF to WCl_6 produces an unknown molecular weight ring opened THF polymer probably *via* a tungstasiloxane intermediate. Given the paucity of information relating to well defined tungsten catalysts it is envisaged that further studies may include a comparison of the potential catalytic activity of $[W(O)\{O(Ph_2SiO)_3\}_2\cdot THF]$ with that of other active tungsten moities. This work should include the active but uncharacterised species derived from the *in situ* reactions of WCl_6 and $[W(O)Cl_4]$, as well as the siloxide complexes described in the literature and in this thesis.

7. Extending the array of model binuclear complexes: Our initial attempts to replace the bridging acetate groups in $[Mo_2(O_2CCH_3)_4]$ failed, mainly because of the insoluble and unreactive nature of the starting material. Consequently it is recommended that future work should involve precursor complexes displaying both higher reactivity and solubility For example $[Mo_2(O_2CCH_3)_4]$ may be reacted with neat ethylenediamine (en) to yield $[Mo_2(O_2CCH_3)(en)_4][(O_2CCH_3)]\cdot en$.

   The product keeps intact the quadrupoly bonded $\{Mo_2\}^{4+}$ unit with spanning ethylenediamine ligands, whilst displaying higher solubility in polar solvents and activation of the complex towards reactions with external organic substrates.[238b] Organo-derivatives of the $\{Mo_2\}^{4+}$ unit should also provide access to binuclear species containing more facile ligands than the unreactive tetracetate compound.

$$[Mo_2(O_2CCH_3)_4] + 8\ LiCH_3 \rightarrow Li_4[Mo_2(CH_3)_8] + 2\ (C_2H_5)_2O$$

The reaction of several group IV metals alkyl complexes with silanols has resulted in the production of metal containing siloxanes with the driving force being the liberation of methane.[285]

5.2.2 CROWN-SILANOL COMPLEXES

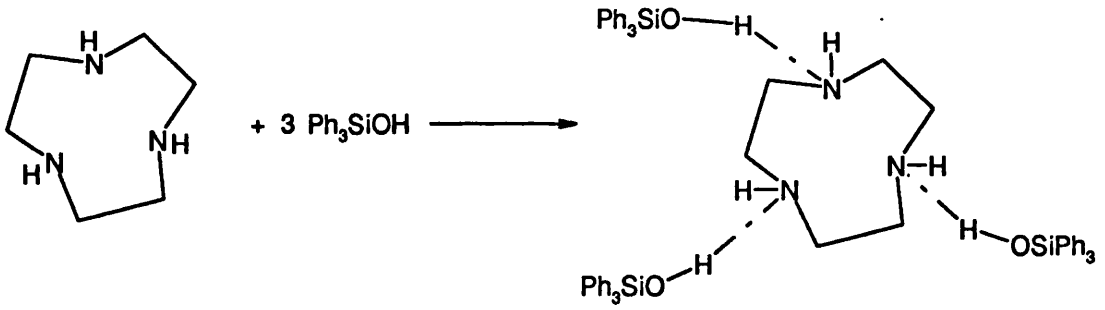
The limited solution and structural studies of crown-silanol complexes undertaken in this thesis should provide a foundation for additional studies in this area. Future work may concentrate on examining the potential of silanol compounds to act as sequestering agents for the selective removal of highly expensive crown compounds from a variety of organic solvents as well as enabling a comparison with the established host-guest chemistry of crown ethers. In order to achieve this goal, the following list of concepts may provide useful starting points in determining the selectivity and affinity of silanols for oxa- (and aza-) crown ethers.

8. Binary crown ether-silanol structures: The spectroscopic data obtained from this project should be consolidated by further crystallographic studies. It is expected that an assessment of bond distances in the triphenylsilanol adducts of 18-crown-6 and diazacrown would consolidate previously collected bond data from this investigation and other studies, *i.e.* $(Ph_3SiOH)_2$·12-crown-4.

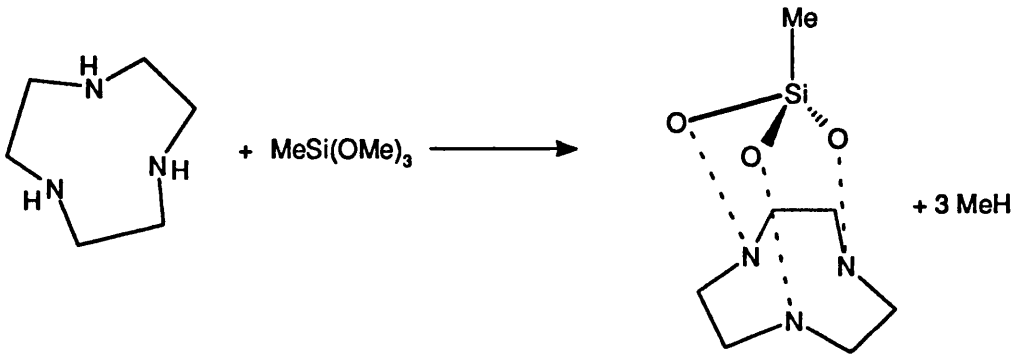
9. Investigate the relationship between the size of the crown ether and the number of co-ordinated triphenylsilanol guests: Although the product $(Ph_3SiOH)_3$·18-crown-6 has been spectroscopically characterised, there is to-date no x-ray crystallographic evidence that more than two silanols guests will co-ordinate to a single oxa- (or aza-) crown ether (up to a ring size of 6 donor atoms). Thus in reactions where large crown ethers (20-crown-6, 21-crown-7, and 28-crown-8) have been utilised potentially larger quantities of sequestering agent may be required to recover the crown from the liquid effluent.

10. The relationship between the bulk of the guest and the number of silanols co-ordinated to the host: For a crown of a given size, decreasing the size of the organic substituents attached to the silicon centre of the silanol should reduce the interactions between co-ordinated guest molecules and hence allow a greater number of silanols to be attached to the host. Thus it may be possible to co-ordinate three or more guests of the type R_3SiOH, where R = Me, Et, Pr.

11. Increasing the number of crown donor (nitrogen) atoms: The synthesis of $(Ph_3SiOH)_2$·monoaza-18-crown-6·(H_2O) and $(Ph_3SiOH)_2$-diaza-18-crown-6 have already demonstrated the preference of triphenylsilanol to bind at the more basic nitrogen site of aza-crown ethers. It is therefore anticipated that the aza-crown, tricyclononane may be able to bind three triphenylsilanol groups at its donor sites.



Triazacyclononane may also be reacted with alkoxysilanes in an attempt to model the highly reactive organotrisilanol species, and in particular, $MeSi(OH)_3$,



12. Linking crowns using bidentate silanols: Previous studies of substituted phenols containing two hydroxy groups have indicated that large supramolecular structures are built up if the spacing between the two groups is wider than 5Å. In attempting to investigate whether similar arrays are produced with silanols, $Ph_2Si(OH)_2$ and $[Ph_2Si(OH)]_2$ have been reacted with 18-crown-6, monoazacrown and diazacrown. Examination of infra-red data obtained suggests that co-ordination of the silanol and crown has occurred but product separation has been problematic. Further work should continue to address this problem through attempting recrystallisations from a wider array of solvent mixtures. This should enable an examination of the relationship, if any, between the structures of the disilanol-crown ether, and phenol-crown ether complexes to be completed.

13. Increasing the denticity of the silanol (siloxane): The addition of 18-crown-6 to Fehers trisilanol compound (**1**) may result in the formation of a 1:1 host:guest compound in which the crown ether sits above the silanol and is linked *via* hydrogen bonds to the three acidic protons of the silanol.

5.2.3 TRANSITION METAL - OXA- AND AZA- CROWN COMPLEXES

The potential to tailor the lability of a macrocycle tethered to a metal entity as well as define the stability of a low oxidation state early transition metal simply by altering the number and type of do-

nor atoms on the macrocycle ring renders them of significant interest in catalytic investigations. It is anticipated that additional studies may be loosely divided into two subsections, the first concentrating on the synthesis and investigation of the catalytic activity of $[Mo(CO)_4(L)_2]$ species where M = Cr, Mo, W and L = oxa-, and aza- crown ether. The section section would consist of using stabilising crown ethers (such as diazacrown or triazacyclononane) to isolate and characterise potential intermediates involved in the catalytic cycles of $[M(CO)_4(L)_2]$, $[M(CO)_3(L)_3]$ and $[M(\eta^3\text{-}C_3H_5)(CO)_2(L)_3]$ complexes where M = Cr, Mo and W. More specific examples arising from this thesis may include:

14. Instigate catalytic investigations: Attempt to assess the reactivity and regioselectivity of the prepared complexes in a manner similar to that discussed for $Mo(CO)_6$, $[Mobipy(CO)_4]$ and related complexes.

15. Extend the range of transition metal $\eta^3\text{-}C_3H_5$ complexes: The generation of $[M(CO)_4(L)_2]$ complexes *via* a ligand displacement reaction similar to that utilised in the synthesis of $[Mo(CO)_4(diazacrown)]$ should provide a suitable entry into a wide range of early transition metal precursors. Subsequent oxidative addition with a suitable allyl compound should provide an opportunity to study potential intermediates in the catalytic cycle of both $[Mo(CO)_4(L)_2]$ and $[Mo(\eta^3\text{-}C_3H_5)(CO)_2]$ complexes.

16. Improve the solubility of $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2]_2$·(diazacrown): Replacing the chloride ligand with a more soluble derivative, *e.g.* ^-SNC or CF_3COO^-, may enable NMR and crystallography studies to be undertaken, and hence confirm the viability of cation molybdenum(allyl) dicarbonyl units as intermediate species.

17. Completing structure of $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(triazacrown)]^+PF_6^-$: To date crystals of sufficient quality to resolve the structure of the PF_6^- counterion have yet to be produced. Replacing the PF_6^- counterion with BF_4^- using the potassium and ammonium salts only resulted in the formation of twinned crystals. In order to overcome this problem a wider range of counterions, including SF_6^- and BPh_4^-, should be investigated.

18. Stabilise the cation with different donor atoms: If aza- crown and crown ether compounds prove unsuitable for stabilsing the reactive transition metal centre then the donor atoms could be replaced with centres more amenable to forming bonds with early transition metal centres. Thus phosphorus (phospha) crown complexes may be substituted for aza- crown compounds, however this in turn may reduce the lability of the ligands to such an extent that catalysis may no longer take place.

Chapter Six: Experimental Details

6.1 SUMMARY

This section describes the synthesis and characterisation of a range of air sensitive model tungsten(oxo) siloxides. $Ph_3SiONa{\cdot}THF$ (S8) was synthesised by direct combination of silanol and sodium metal in THF. $[W(O)Cl_4]$ reacted with 3 or 4 equivalents of (S8) to yield the extremely air and moisture sensitive $[W(O)Cl(OSiPh_3)_3]$ (P1). Metal-halide metathesis reactions were employed to synthesise $[W(O)_2(OSiPh_3)L]_2$ where L = DMSO (P3) or $OPPh_3$ (P4) and $[W(O)_2(OSiPh_3)_2L_2]$ where L = TMSO (P2). The effect of ring size in the reactions of tungsten(oxo) halides and cyclosiloxanes was investigated and the synthesis and characterisation of a novel, air stable, spirosiloxane, $[WO\{O(OSiPh_2)_3\}_2{\cdot}THF]$ (P6) is described. The compound $[W(O)\{OSiPh_2O\}_2]$ (P8) was sucessfully synthesised *via* a metal-halide metathesis reaction but attempts to generate (P6) employing this route were unsuccessful.

The ability of silanols, oxa- and aza- crown ethers to form complex H-bonded compounds has been well documented and further investigations have led to the synthesis and characterisation of $(Ph_3SiOH)_3{\cdot}$18-crown-6 (C3), $(Ph_3SiOH)_2{\cdot}$18-crown-6$\cdot(H_2O)_2$ (C4), $(Ph_3SiOH)_3{\cdot}$18-crown-6$\cdot(H_2O)_3$ (C5), $(Ph_3SiOH)_2{\cdot}$monoazacrown$\cdot(H_2O)$ (C6), $(Ph_3SiOH)_2{\cdot}$diazacrown (C7). Also reported are the modified literature preparations for the more efficient syntheses of 1-aza-18-crown-6 (C1) and 7,16-diaza-18-crown-6 (C2).

A range of crown ether-early transition metal complexes that may function as potential homogeneous catalysts were synthesised. Thus the preparation of $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)]_2{\cdot}$(diazacrown) (MC1), $[Mo_2(CO)_6$(diazacrown)] (MC2) and $[Mo(CO)_4$(diazacrown)] (MC4) are reported, attempts to synthesise the chromium (MC3) analogue are also detailed. The macrocycle, 1,4,7-triazacyclononane was complexed with $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$ and NH_4PF_6 in a one pot reaction to yield $[Mo(\eta^3\text{-}C_3H_5)(CO)_2$(triazacrown)$]PF_6$ (MC5). Crystallography confirmed the structure of the cation however a complete solution was not possible due disorder within the counterion. In an attempt to find a complete structure (MC5) was also prepared in single pot reactions using KPF_6 and KBF_4, unfortunately the crystals obtained were twinned.

Literature preparations leading to the syntheses of a range of substituted silanol and siloxane compounds are described, as are those concerning the preparation of the metal(oxo)chlorides.

6.2. SYNTHETIC TECHNIQUES

Unless stated all manipulations were carried out in an atmosphere of dried, purified nitrogen using standard Schlenk and cannula techniques. Inert atmosphere techniques were achieved using a standard gas/vacuum line with rotatable 2 way stopcocks. Preparation of model silanols was carried out under normal atmospheric conditions in dried glassware. Glassware was dried in a hot box oven overnight at 120°C prior to use and flame dried under vacuum if necessary.

6.2.1. REAGENTS

Hexamethyldisiloxane (99.9%+, NMR grade), tungsten hexachloride, molybdenum hexacarbonyl, allyl chloride, rhenium pentachloride, dimethylsulphoxide, tetramethylenesulphoxide, triphenylphosphine oxide, hexaphenylcyclotrisiloxane, octaphenylcyclotetrasiloxane, triphenylsilanol, diphenylsilanediol, 18-crown-6 were purchased from Aldrich Chemical Company and used as supplied. 1-aza-18-crown-6 and 7,16-diaza-18-crown-6 were initially purchased from Aldrich Chemical Company but were also synthesised by a modified literature procedure. Sodium carbonate was also obtained from Aldrich Chemical Company and dried overnight at 130°C before use.

Liquid reagents were distilled and stored under nitrogen over 4Å molecular sieves whilst solvents were freshly distilled under nitrogen. Toluene, THF, hexane, octane and diethyl ether were dried by reflux over sodium and benzophenone. Dichloromethane and 1,2-dichloroethane were heated to reflux over calcium hydride and fractionated before use. Pentane and petroleum ether 60-80° were distilled over sodium and benzophenone prior to use and stored over 4Å molecular sieves.

6.2.2. SAMPLE ANALYSIS

Infrared spectra were recorded as nujol mulls on a Nicolet 570P FTIR and a Perkin-Elmer IR spectrophotometer using NaCl or CsI plates. Peaks are reported as (ν_{max}) wavenumbers (cm^{-1}).

NMR measurements were obtained on JEOL GX 270 MHz and JEOL EX 400 MHz FT spectrometers. Unless otherwise stated all spectra were obtained at room temperature. ^{1}H chemical shifts are reported in units of ppm downfield from tetramethylsilane (TMS). $^{13}C\{^{1}H\}$ chemical shifts were measured relative to residual ^{13}C in the deuterated solvents. ^{29}Si chemical shifts are reported relative to TMS, samples contained 0.02M $Cr(acac)_3$ to ensure integrated intensities through the reduction of T_1's.

Microanalysis was performed where relevant by Mr A Carver on a Carlo Erba 1106 Elemental Analyser at the University of Bath. No special precautions were taken during the analysis and conse-

quently some hygroscopic samples indicate the presence of coordinated water. Mass spectra were obtained by Mr C Cryer on a VG Analytical 7070E Quadrupole Mass Spectrometer.

Single crystal x-ray diffraction studies were undertaken by Dr M.F. Mahon at the University of Bath using a CAD4 automatic 4 circle diffractometer. Parameters for individual structures are reported in the relevant appendices.

6.3 LITERATURE PREPARATIONS

6.3.1. METAL COMPLEXES

Preparation of $[W(O)Cl_4]$ (M1)[108]

A solution of $(Me_3Si)_2O$ (2.2g, 13.4 mmol) in 25 ml of dichloromethane was added dropwise at room tempertaure to a vigorously stirred suspension of WCl_6 (5.3g, 13.4 mmol) in 15 ml of dichloromethane over a period of 15 min. An immediate reaction ensued leading to the formation of tiny red crystals and a viscid liquor. The mixture was stirred for a further 60 min and the crystals of $[W(O)Cl_4]$ decanted from the supernatant liquor, washed with 60–80° petroleum ether (2 × 10 ml) and cautiously dried *in vacuo* to yield the title product (4.3g, 94%). Faster addition of the hexamethyldisiloxane solution deposits $[W(O)Cl_4]$ as an amorphous orange powder.

IR 956, 892, 873, 812, 783, 669, 642, 390, 372, 350, 325, 305, 280 cm^{-1}.

Preparation of $[W(O)_2Cl_2]$ (M2)[108]

A solution of $(Me_3Si)_2O$ (0.6g, 3.8 mmol) in 6 ml of octane was added dropwise to a vigorously stirred suspension of $[W(O)Cl_4]$ (1.3g, 3.8 mmol) in 20 ml of octane. Upon completion of the addition the suspension was placed in an oil bath preheated to 45°C and the temperature increased rapidly to 80°C. Stirring was continued for approximately 4.5 hours until the orange colouration of the solid was discharged to leave a yellow solid and a colourless solution. After cooling to room temperature the solid was decanted from the supernatant liquor and washed with 60–80° petroleum ether (2 × 5 ml). Cautious drying *in vacuo* yielded the title product (0.61g, 56%). Exposure to air or moisture resulted in the formation of a grey powder.

IR 840, 816, 740 cm^{-1}.

Preparation of $[W(O)_2Cl_2(DMSO)_2]$ (M3)[208a]

A solution of WCl_6 (1.5g, 3.8 mmol) in 30 ml of acetone was added dropwise to a solution of 3 ml of $(CH_3)_2SO$ in 10 ml of acetone. Upon gentle shaking the green solution became brown and deposited white crystals. After standing at 0°C for 1 hour, buchner filtration and washing with ice cold acetone

(2 × 5 ml) and ether (2 × 5 ml) followed by air drying yielded the title product (1.1g, 66%, mpt 80°C).

Analysis (calculated for $C_4H_{12}Cl_2O_4S_2W$) Found C 10.8 (10.8), H 2.87 (2.74) %; IR 1036, 997, 988, 955, 916, 893 cm^{-1}.

Preparation of $[W(O)_2Cl_2(TMSO)_2]$ (M4)[208a]

A freshly prepared solution of WCl_6 (2.0g, 5.04 mmol) in 20 ml of acetone was added dropwise to a solution of 5 ml of $(C_4H_8)SO$ in 20 ml of acetone. Upon gentle agitation the green solution became brown and deposited white crystals. After 3 hours standing at 0°C, the solid was filtered off, washed with cold acetone (2 × 10 ml), ether (2 × 10 ml) and air dried. Yield (1.6g, 64%).

Analysis (calculated for $C_8H_{16}O_4Cl_2S_2W$) Found C 19.6 (19.4), H 3.27 (3.26) %; IR 1460, 1402, 1304, 1001, 976, 947, 930, 899, 779, 723, 667 cm^{-1}.

Preparation of $[W(O)_2Cl_2(OPPh_3)_2]$ (M5)[208a]

To a stirred solution of WCl_6 (2.0g, 5.0 mmol) in 20 ml of acetone was added, dropwise, 40 volume hydrogen peroxide just sufficient to discharge the green colouration. This solution was added dropwise to a freshly prepared solution of $(C_6H_5)_3PO$ in 20 ml of acetone. White crystals deposited upon standing at 0°C for 1 hour. The title product was filtered, washed with acetone (2 × 15 ml) and ether (2 × 15 ml) and air dried (2.4g, 57%, mpt 278-280°C).

Analysis (calculated for $C_{36}H_{30}Cl_2O_4P_2W$) Found C 51.0 (51.3), H 3.5 (3.6); IR 1590, 1485, 1314, 1140, 1119, 1086, 1030, 997, 959, 913, 851, 752, 723, 693 cm^{-1}.

Preparation of $[Mo_2(O_2CCH_3)_4]$ (M6)[240]

A mixture of molybdenum hexacarbonyl (4.2g, 15.9 mmol) and glacial acetic acid (20 ml) in 85 ml of acetic anhydride was refluxed under a constant stream of nitrogen for 4 hours. Cooling the mixture to room temperature followed by immersion in a salt ice bath for 30 minutes resulted in the precipitation of a green solid which was filtered in a Buchner funnel and washed successively with two 10 ml portions of cold ethanol and diethyl ether before being air dried to yield the product (1.3g, 19%) as fine needles.

Analysis (Calculated for $C_8H_{12}O_8Mo_2$). Found C 23.5 (23.4), 2.1 (2.3); IR 1511, 1495, 1412, 1048, 1032, 936, 677, 446, 426 cm^{-1}.

Preparation of $K_4[Mo_2Cl_8]$ (M7)[240]

Finely powdered potassium chloride was added to 50 ml of fresh concentrated hydrochloric acid to produce a saturated solution, the excess solid was filtered off in a glass sinter. Dimolybdenum(II) acetate (1.0g, 2.3 mmol) was added with stirring to the filtrate and the mixture left for 30 minutes in a stoppered flask. The red suspension was filtered using a sintered glass crucible and the product collected (1.0g, 66%) and washed successively with two 15 ml portions of ethanol and diethyl ether before being air dried.

IR 304, 278 cm^{-1}.

Preparation of $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$ (M8)[261,286]

A 100 ml round bottomed flask containing 50 ml of acetonitrile was charged with $[Mo(CO)_6]$ (5.0g, 18.9 mmol) and excess (10 ml) C_3H_5Cl. The suspension was heated under reflux for 20 hours to yield an orange solution which was then cooled slightly and the solution evaporated to low bulk. Cooling in ice for 30 minutes precipitated an orange solid which was filtered at the pump under a blanket of nitrogen, washed with a little cold acetonitrile (2 × 10 ml) and cautiously dried to yield the title product (5.2g, 88%)

Analysis (calculated for $C_9H_{11}ClN_2O_2Mo$) Found C 35.0 (34.8), H 3.53 (3.57), N 9.00 (9.07) %; IR 2317, 2284, 1948, 1855, 1177, 1024, 961, 899, 799, 635 cm^{-1}; ^1H NMR (ppm, CD_3OD) 1.11 (2H, d, $CH_aH_sCHCH_aH_s$), 2.04 (6H, s, CH_3CN), 3.41 (2H, d, $CH_aH_sCHCH_aH_s$), 3.65 (1H, s, $CH_aH_sCHCH_aH_s$), ^{13}C NMR (ppm, CD_3OD) 1.2 (CH_3CN), 50.2 (CH_2CHCH_2), 59.9 (CH_3CN), 74.4 (CH_2CHCH_2).

Preparation of $[MoC_7H_8(CO)_4]$ (M9)[287]

A 1 litre, 3 neck round bottomed flask fitted with a reflux condenser, mechanical stirrer and pressure equalising dropping funnel was flushed with nitrogen and charged with $Mo(CO)_6$ (5.26g, 19.92 mmol) and 40 ml of methylcyclohexane. The mixture was heated to reflux with stirring and 7.5 ml of bicylcoheptadiene added dropwise over 5 minutes. Refluxing was maintained for 16 hours to yield a dark reddy-brown suspension which cooled to room temperature. Filtration under nitrogen through glass wool stood over a frit gave a clear filtrate which was cautiously reduced to half volume and stored overnight at -30°C. The tan solid precipitated was decanted and dried cautiously. Sublimation of the solid (90°C, 0.01 mmHg) gave the pure title compound as a light yellow solid (0.82g, 14%). The solid became pale brown on standing although no decomposition of the product was detected by IR.

IR 2030, 1980-1920, 1870 cm^{-1}.

6.3.2. SILANOLS AND SILOXANES

Preparation of tetramethyldisiloxane-1,3-diol, disodium salt (S1)[8]

To octamethylcyclotetrasiloxane (50g, 169 mmol) was added 54g of 50% aqueous sodium hydroxide (52 mmol). The mixture was stirred while 20 ml of methanol was added and then heated gradually until boiling at which stage small portions of methanol were added until the mixture became homogeneous. After allowing the mixture to cool slightly water suction was applied to remove solvent and uncombined water and afford a white powder. The powder represents essentially a quantitative yield of the pentahydrate which was recrystalised twice from hot acetone to yield the title product.

Analysis (Calculated for $C_4H_{22}O_8Na_2Si_2$) Found C 17.5 (16.0) H 7.9 (7.3) %; IR 3656, 3636, 1258, 986, 851, 783, 669, 646, 592 cm^{-1}

Preparation of tetramethyldisiloxane-1,3-diol (S2)[8]

To a solution of fresh glacial acetic acid (3.4g, 56.6 mmol) in 175 ml of diethyl ether was added with good stirring and in small portions the finely powdered tetramethyldisiloxane-1,3-diol, disodium salt (8.5g, 28.3 mmol). Upon dissolution of the sodium salt a fine white precipitate of insoluble sodium acetate appeared. The course of the reaction was monitored using litmus and universal indicator paper until the neutral point was reached (CARE addition of the last 20% of the sodium salt should be done very cautiously as the product cyclises in contact with only minute quantities of base). The solid sodium acetate was removed by filtration and the ether layer evaporated to yield a mixture of oil and crystalline needles. Washing with light petroleum ether freed the crystals from the oil to yield title product (2.2g, 46%, mp 59°C).

Analysis (Calculated for $C_4H_{14}O_3Si_2$) Found C 28.9 (28.9) H 8.58 (8.50) %; IR 3206, 1410, 1262, 1024, 864, 783, 656, 556 cm^{-1}; ^1H NMR (ppm, $CDCl_3$) 0.121, 0.123 (12H, m, CH_3), 0.34 (2H, bs OH); ^{13}C NMR (ppm, $CDCl_3$) 0.19 (CH_3); ^{29}Si NMR (ppm, $CDCl_3$, $Cr(acac)_3$) -10.3

Preparation of heptacyclohexyl-heptasiloxane-1,6,7-triol (S3)[16]

Distilled water (125 ml) was carefully added with stirring to cyclohexyltrichlorosilane (25g, 0.11 mol) dissolved in 500 ml of acetone and the mixture allowed to stand at room temperature for 4 months.

To ease filtration most of the solvent and the resinous material were first decanted before the white crystalline precipitate was filtered using a Buchner funnel. It was then washed with 30 ml of cold acetone to dissolve any remaining resin. The washings were returned to the reaction vessel and the remaining white solid dried overnight at 40-50°C. The 1.7g of crude material collected contained an

approximate 2:1 of heptacyclohexyl-heptasiloxane-1,6,7-triol (S3) and hexacyclohexyl-hexasiloxane (S4).

Product (S4) was isolated by stirring the crude mixture with 5 times it weight of pyridine for 1 hour and filtering the remaining solid in a Buchner funnel. The quantitative amount of microcrystalline solid material collected was washed with a small amount of pyridine and dried overnight at 25°C. Recrystallisation of the material from boiling chloroform afforded the pure material (0.4g, 0.5%, mp 235°C).

Analysis (calculated for $C_{36}H_{66}O_9Si_6$) Found C 52.9 (53.2) H 8.38 (8.21) %; IR 1227, 1196, 1044, 997, 895, 859, 785, 762, 754, 641, 627, 571, 527, 465, 473 cm^{-1}; ^1H NMR (ppm, $CDCl_3$) 1.74 (36H, m), 1.26 (24H, m), 0.84 (6H, m); ^{13}C NMR (ppm, $CDCl_3$) 27.6, 26.9, 26.5 (CH_2), 22.9 (CH); ^{29}Si NMR (ppm, $CDCl_3$, $Cr(acac)_3$) -56.6

Isolation of (S3) was accomplished by pouring the pyridine extract from (S3) carefully into 5 times its volume of ice-cold aqueous hydrochloric acid (1 ml of concentrated HCl/ ml of pyridine). Any large clumps of precipitated product were pulverised and the white precipitate filtered using a buchner funnel. The solid was then stirred in a large excess of water to remove any mechanically entrained pyridine, pyridium hydrochloride or hydrochloric acid. The product was collected on a Buchner funnel and washed with copious amounts of water before being dried overnight at 40-50°C. Dissolving the material in hot diethyl ether (30 ml/g of 3) and filtering removed any particulates, concentration of the solvent to approximately 25% of the original volume yielded analytically pure (3) (3.9g, 29%, mp 256°C).

Analysis (calculated for $C_{42}H_{80}O_{12}Si_7$). Found C 51.8 (51.8) H 8.47 (8.30) %; IR 1449, 1269, 1194, 1129, 1038, 1026, 997, 920, 893, 849, 752, 480, 473, 407 cm^{-1}; ^1H NMR (ppm, $CDCl_3$) 0.72 (7H, bs, C_6H_{12}), 1.23 (35H, s, C_6H_{12}), 1.72 (35H, s, C_6H_{12}), 6.99 (3H, s, SiO*H*); ^{13}C NMR (ppm, $CDCl_3$) 26.7, 26.9, 27.6 (CH_2), 23.2, 23.6, 24.0 (*C*H); ^{29}Si NMR (ppm, $CDCl_3$, $Cr(acac)_3$) -60.5, -68.2, -69.8;

Preparation of tetraphenyl-1,3-dihydroxydisiloxane (S5)[8, 11]

Dichlorodiphenylsilane (30.1g, 118.9 mmol) was added dropwise during 1 hour to a suspension of ammonium carbonate (16.0g, 166.5 mmol), water (2.2g, 122.2 mmol) and 170 ml of freshly distilled ether stirred using a modified Hershberg stirrer. The mixture was then boiled under reflux for 12 hours and then stirred with 80 ml of water prior to the ether phase being separated. The aqueous phase was extracted three times with 75 ml portions of ether and the extracts combined and dried over anhydrous magnesium sulphate. Evaporation of the ether left a white residue which was extracted 5 times with cold benzene (CARE) to remove the insoluble diphenylsilanediol (S6) (3.1g,

12%, mp 156°C) from the oligomeric siloxanols and cyclic siloxanes which were recovered on evaporation of the combined extracts.

Analysis (calculated for $C_{12}H_{12}O_2Si$) Found C 66.6 (66.6), H 5.4 (5.6) %; IR 1429, 1333, 1130, 1121, 907, 882, 839, 720, 698, 509, 490, 475 cm^{-1}; ^{29}Si NMR (ppm, $CDCl_3$) -33.4

Washing the residue successively with a 1:5 and a 1:1 benzene/petrol mixture yielded crude tetraphenyldisiloxane-1,3-diol which was recrystallised from a 5:1 benzene/petrol mixture to yield the analytically pure product (S5) (11.8g, 48%, mp 114°C).

Analysis (calculated for $C_{24}H_{22}O_3Si_2$) Found C 69.2 (69.5), H 5.22 (5.36) %; IR (KBr plates, nujol mull) 1429, 1306, 1265, 1190, 1127, 1082, 1028, 997, 887, 851, 739, 718, 696, 631, 615, 513, 484 cm^{-1}; ^1H NMR (ppm, $CDCl_3$) 3.99 (2H, bs, O*H*), 7.23-7.59 (20H, m, C_6H_5); ^{13}C NMR (ppm, $CDCl_3$) 127.5, 130.3, 134.3 (C_6H_5); ^{29}Si NMR (δppm, $CDCl_3$, $Cr(acac)_3$) -35.9;

Preparation of di-t-butyltetrahydroxydisiloxane (S7)[10,14]

Tertiary butyl trichlorosilane (7.8g, 40.7 mmol) in 55 ml of ether was added dropwise with stirring over a period of 20 minutes to an ice cold solution of potassium hydroxide (6.9g, 123 mmol) in 50 ml of ether, 5 ml of methanol and 40 ml of water. The solution became acidic (monitored using pH paper) and so a fourth equivalent of potassium hydroxide was added and stirred into the mixture for 25 minutes to render the solution alkaline. The organic phase was separated and the aqueous phase extracted three times with diethyl ether, the extracts were combined and evaporated at reduced pressure to yield a white solid which was recrystallised from acetone (6.9g, 59%, mp 177-212°C).

Analysis (calculated for $C_8H_{22}O_5Si_2$). Found C 37.8 (37.8) H 9.06 (8.66) %; IR (KBr plates, nujol mull) 3120, 1190, 1128.5, 1009, 934, 895, 866 cm^{-1}; ^1H NMR (ppm, CD_3OD) 0.99 (18H, s), 4.91 (4H, s); ^{13}C NMR (ppm, CD_3OD) 18.2 $C(CH_3)_3$, 26.7 $C(CH_3)_3$;^{29}Si NMR (δppm, CD_3OD, $Cr(acac)_3$) -49.53

6.4 REACTIONS

6.4.1 CROWN SUPPORTED MOLYBDENUM COMPLEXES

Preparation of $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)]_2$·(diazacrown-6) (MC1)

Solid $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$ (0.60g, 1.93 mmol) was added with vigorous stirring to a 100 ml round bottomed flask charged with 45 ml of acetonitrile. The mixture was warmed to 45°C to effect dissolution and diazacrown (0.51g, 1.93 mmol) added in portions to form a yellow precipitate. Stirring was maintained for a further 30 minutes, the suspension cooled slightly, and the solvent

evaporated to low bulk. The resulting solid was filtered at the pump, washed with cold acetonitrile (1 × 10 ml) and dried to yield the title product as a fine yellow powder (0.7g, 74%).

With the exception of acetone in which it was very sparingly soluble compound (**MC1**) was found to be insoluble in all common organic solvents with which it did not react. Washing with organic solvents, prolonged drying or storage over the period of a week resulted a greeny-brown solid which contained no acetontrile. It otherwise displayed good stability. In solution on exposure to air the compound decomposed to yield a brown suspension containing no detectable (*via* IR) carbonyl functions.

Analysis (calculated for $C_{26}H_{42}Cl_2N_4O_8Mo_2$) Found C 38.9 (38.9), H 5.18 (5.37), N 6.86 (7.14) %; IR 3231, 1919, 1821, 1468, 1453, 1298, 1132, 1074, 1053, 1040, 1003, 909, 862, 804, 641.

Synthesis of $[Mo_2(CO)_6$·(diazacrown)] (MC2)

A 100 ml round bottomed flask was charged with $[Mo(CO)_6]$ (0.23g, 0.88 mmol) and diazacrown (0.23g, 0.88 mmol). Toluene, 30 ml, was added and the mixture heated under reflux for 2 hours to yield a pale brown solid suspended in a yellow solution. The solution was cooled in ice for 2 hours and filtered at the pump to yield a brown solid. The solid was washed with pentane (2 x 5 ml) and air dried to yield the title compound (0.31g, 57%).

Compound (**MC2**) was stable as a solid but it was insoluble in all common organic solvents except DMSO in which it showed good solubility. The compound was stable in solution overnight under nitrogen but decomposed with the loss of the carbonyl functions on exposure to air.

Analysis (calculated for $C_{18}H_{26}N_2O_{10}Mo_2$) Found C 34.7 (34.8), H 4.60 (4.22), N 4.83 (4.61) %; IR 3322, 3273, 1908, 1790, 1736, 1129, 1078, 1069, 1055, 978, 965, 830 cm^{-1}. ^1H NMR (ppm, d_6-DMSO) 3.04 (br s, 8H, $CH_2CH_2NHCH_2CH_2$), 3.65 (s, 8H, OCH_2CH_2O) 3.92 (br s, 8H, OCH_2CH_2O); ^{13}C NMR (ppm, d_6-DMSO) 47.9 ($CH_2CH_2NHCH_2CH_2$), 67.7, 69.4 (OCH_2CH_2O).

Attempted synthesis of $[Cr(CO)_2$(diazacrown)] (MC3)

A schlenk tube was charged with $[Cr(CO)_6]$ (0.25g, 1.14 mmol), diazacrown (0.30g, 1.14 mmol), 10 ml of toluene was added and the mixture heated in the dark under reflux for 6 hours. Cooling in ice and reducing the volume of solvent to a third of its original gave an orange solid. The solvent was decanted and the product washed with ether (2 × 5 ml) and dried in vacuo to yield an orange solid (0.41g, 79%). The product was found to be stable in chloroform and dichloromethane solutions overnight but decomposed rapidly on exposure to air.

Analysis (calculated for $C_{14}H_{26}N_2O_6Cr$) Found C 52.1 (45.4), H 8.70 (7.09), N 8.27 (7.61) %; IR 3335, 1977, 1908, 1351, 1331, 1287, 1250, 1154, 1129, 1107, 1073, 976, 841 cm^{-1}. ^1H NMR

(ppm, $CDCl_3$) 2.82 (8H, br s, $CH_2CH_2NHCH_2CH_2$), 3.63 (16H, br s, $CH_2CH_2OCH_2CH_2$); ^{13}C NMR (ppm, $CDCl_3$) 49.5 ($CH_2CH_2NHCH_2CH_2$), 70.4 ($CH_2CH_2OCH_2CH_2$), 208.4 (*CO*)

Synthesis of [Mo(CO)$_4$·(diazacrown)] (MC4)

A schlenk tube was charged with [$Mo(CO)_4C_7H_8$] (0.26g, 0.86 mmol) and 15 ml of dichloromethane added to give a light yellow solution. To this vigorously stirred solution was added dropwise a solution of diazacrown (0.23g, 0.86 mmol) in 3 ml of dichloromethane. Stirring was continued for 4.5 hours and the solvent removed *in vacuo* to yield the title product as a yellow solid (0.38g, 93%).

Compound (MC4) was stable as a solid under nitrogen but decomposed on exposure to air to yield a red solid. It was found to be soluble in polar organic solvents but decomposed rapidly in solution on exposure to moisture to yield a brown solid containing no carbonyls.

Analysis (calculated for $C_{16}H_{26}N_2O_8Mo$) Found C 40.6 (40.8), H 5.80 (5.58), N 5.82 (5.99) %; IR (nujol mull) 3216, 2008, 1879, 1852, 1802, 1289, 1248, 1119, 1109, 1154, 1084, 1055, 995 cm^{-1}; ^1H NMR (ppm, CD_2Cl_2) 2.86 (t, 8H, $CH_2CH_2NHCH_2CH_2$, J = 4.6 Hz), 3.66 (s, 16H, OCH_2CH_2O), ^{13}C NMR (ppm, CD_2Cl_2) 49.8 ($CH_2CH_2NHCH_2CH_2$), 70.6 (OCH_2CH_2O).

Synthesis of [Mo(η^3-C_3H_5)(CO)$_2$(1,4,7-triazacyclononane)PF_6] (MC5)[280, 288]

[$MoCl(\eta^3$-$C_3H_5)(CO)_2(NCMe)_2$] (0.60g, 2.0 mmol) and KPF_6 (0.70g, 3.8 mmol) were dissolved in 35 ml of acetonitrile. The mixture was stirred and heated under reflux for one hour and upon cooling to room temperature an orange solid was formed. The solid was decanted from the liquor and washed with small amounts of cold acetonitrile (2 × 5 ml) and ether (2 × 5 ml) to yield the title product (0.54g, 86%). Reduction of the filtrate to two-thirds its initial volume and storage in a refridgerator for four weeks yielded small orange crystals of (MC5) which were suitable for crystallography. Further examination of these crystals showed these to be twinned.

Analysis (calculated for $C_{11}H_{20}N_3MoPF_6$) Found C 26.5 (26.3), H 4.15 (3.98), N 8.43 (8.36) %; IR 3424, 3327, 2363, 1933, 1850, 1653, 1092, 1047, 959, 835 cm^{-1}; ^1H NMR (ppm, CD_3CN) 1.14 (2H, d, J = 11 Hz, $CH_aH_sCHCH_aH_s$), 2.65 (2H, d, J = 8 Hz, crown), 3.14 (10H, s, crown), 3.15 (2H, d, J = 7 Hz, $CH_aH_sCHCH_aH_s$), 3.61 (1H, sept, $CH_aH_sCHCH_aH_s$); ^{13}C NMR (ppm, CD_3CN) 48.7 (CH_2CHCH_2), 54.0 (*crown*), 70.5 (CH_2CHCH_2), 206.3 (*CO*), 238.4 (*CO*)

A BF_4 analogue of (MC5) (prepared as above using KBF_4) also resulted in twinned crystals which defied further attempts at recystallisation from acetone/ether, acetone/hexane and acetone and cyclohexane.

6.4.2 MOLYBDENUM AND TUNGSTEN SILOXIDES AND SILOXANES

Synthesis of $Ph_3SiONa{\cdot}THF$ (S8)

A schlenk tube was charged with freshly cleaned sodium metal (0.69g, 30.0 mmol) and 40 ml of THF and cooled to 0°C. A solution of Ph_3SiOH (5.00g, 18.1 mmol) in 25 ml of THF was added dropwise with vigorous stirring, resulting in the evolution of hydrogen gas from the surface of the metal. Stirring was continued overnight whilst the mixture warmed to room temperature. Unreacted sodium metal was removed by filtration and the volatiles evaporated to yield a crispy white residue which was redissolved in 35 ml of THF, filtered and hexane added so as to form a layer. Large hexagonal crystals of the product unsuitable for a structural determination precipitated at room temperature overnight (6.1g, 87%).

Accurate microanalysis was difficult as the compound readily absorbed water, the analysis presented is for (S8) containing a single coordinated water molecule.

Analysis (calculated for $C_{22}H_{25}O_3NaSi$) Found C 68.1 (68.0), H 6.06 (6.50) %; IR 3129, 3058, 3038, 1426, 1260, 1107, 1053, 1032, 992, 893, 737, 702 cm^{-1}; ^1H NMR (ppm, C_4D_8O) 1.59 (t, 4H,β-CH_2 of THF), 3.45 (t, 4H, α-CH_2 of THF), 6.99 (m, 10H, *meta, para* C_6H_5), 7.37(m, 5H, *ortho* C_6H_5); ^{13}C NMR (ppm, C_4D_8O) 126.8, 128.7, 130.8, 134.4 (C_6H_5)

Synthesis of $[WCl(O)(OSiPh_3)_3]$ (P1)

A solution of Ph_3SiONa (1.02g, 3.42 mmol) in 35 ml of THF was added dropwise to an ice cold, stirred suspension of $[W(O)Cl_4]$ (0.39g, 1.14 mmol) in 20 ml of THF. An immediate reaction ensued with the initial orange suspension fading to a colourless solution which finally became pale blue upon reaching room temperature. Stirring was continued overnight and the volatiles removed *in vacuo* to yield a pale blue residue which was extracted with 75 ml of toluene. The title product was isolated from the filtrate following evaporation of the solvent (1.1g, 91%).

Compound (P1) was hygroscopic but stable as a solid however it rapidly decomposed to yield a blue solution upon exposure to air. The microanalysis below indicates a monhydrate species.

Analysis (calculated for $C_{54}H_{47}ClO_6W$) Found C 60.1 (60.1), H 4.64 (4.40) %; IR 3182, 3069, 3044, 1484, 1428, 1117, 1030, 999, 959, 909, 874, 739, 712, 698 cm^{-1}; ^1H NMR (ppm, C_6D_6) 7.2 (m, 27H, *ortho, para* C_6H_5), 7.7 (m, 18H, *meta* C_6H_5); ^{13}C NMR (ppm, C_6D_6) 136.4, 136.0, 135.8, 131.3, 13 0.5 (C_6H_5).

Reaction of $[W(O)Cl_4]$ with $KOSiMe_3$

A solution of $KOSiMe_3$ (0.45g, 3.51 mmol) in 40 ml of THF was added dropwise to an ice cold, stirred suspension of $[W(O)Cl_4]$ (0.30g, 0.88 mmol) in 25 ml of THF. An immediate reaction ensued and the orange solid dissipated to yield a blue solution. Stirring was continued for 1 hour and the volatiles removed *in vacuo* to yield an off-white solid (0.7g) which was found to be air stable and insoluble in toluene, dichloromethane and diethyl ether.

IR 1561, 1252, 1154, 1049, 900-700(bs), 847 cm^{-1}.

Reaction of $[W(O)_2Cl_2(DMSO)_2]$ with $KOSiMe_3$

A solution of $KOSiMe_3$ (0.41g, 3.2 mmol) in 20 ml of THF was added dropwise to an ice cold, stirred suspension of $[W(O)_2Cl_2(DMSO)_2]$ (0.71g, 1.60 mmol) in 40 ml of THF. The suspension was allowed to warm to room temperature and the stirring continued overnight. Volatiles were removed *in vacuo* to yield a white solid which was found to be insoluble in toluene, dichloromethane and diethyl ether.

IR 1646, 1156, 1024, 950-780(bs), 830 cm^{-1}.

The Synthesis of $[W(O)_2(OSiPh_3)_2(TMSO)_2]$ (P2)

A solution of Ph_3SiONa (1.57g, 5.26 mmol) in 40 ml of THF was added dropwise to an ice cold, stirred suspension of $[W(O)_2Cl_2(TMSO)_2]$ (1.3g, 2.62 mmol). The mixture was allowed to warm to room temperature and stirring was continued overnight. Volatiles were removed *in vacuo* and the residue extracted with 80 ml of toluene. Evaporation of the extract yielded the title product (1.96g, 77%).

Compound (**P2**) is stable as a solid when stored under nitrogen. In solution it decomposes rapidly to yield a brown solution if exposed to air.

Analysis (calculated for $C_{44}H_{46}O_6S_2Si_2W$) Found 54.2 (54.2), H 5.07 (4.76) %; IR 1460, 1428, 1306, 1262, 1186, 1115, 1035, 1022, 1001, 945, 931, 893, 833, 740, 708, 700 cm^{-1}; ^1H NMR (ppm, CD_2Cl_2) 0.9 (m, 4H, C_4H_8SO), 1.9 (m, 4H, C_4H_8SO), 2.3 (m, 4H, C_4H_8SO), 2.7 (m, 4H, C_4H_8SO), 7.1-7.5 (m, 18H, meta, para C_6H_5), 7.8-8.0 (m, 12H, ortho C_6H_5); ^{13}C NMR (ppm, CD_2Cl_2) 25.9, 29.9, 34.2, 37.5 (C_4H_8SO), 127.9 (*meta* C_6H_5), 129.9 (*para* C_6H_5), 136.4 (*ortho* C_6H_5), 137.9 (*ipso* C_6H_5).

Synthesis of $[W_2(O)_4(\mu_2\text{-}OSiPh_3)_2(DMSO)_2]$ (P3)

A solution of Ph_3SiONa (0.66g, 2.34 mmol) in 25 ml of THF was added dropwise to an icecold, stirred suspension of $[W(O)_2Cl_2(DMSO)_2]$ (0.52g, 1.17 mmol) in 25 ml of THF. The mixture was

stirred overnight whilst it warmed to room temperature. Solvent was removed *in vacuo* to yield a white residue which was extracted with 80 ml of toluene to remove soluble products. Evaporation of the volatiles from the filtrate yielded the title product (0.46g, 43%).

The compound was found to be stable as a solid and could be stored under nitrogen for several weeks. Exposure to moisture either as a solid or in solution resulted in the rapid decomposition of the product.

Analysis (calculated for $C_{40}H_{42}O_8S_2Si_2W_2$) Found C 42.4 (42.2), H 3.85 (3.72) %; IR 3065, 3046, 1428, 1119,1028, 999, 995, 945, 889, 862, 837, 741, 711, 700 cm^{-1}; ^1H NMR (ppm, C_6D_6) 1.53 (s, 12H, $(CH_3)_2SO$), 7.16-7.19 (m, 20H, *meta, para* C_6H_5), 7.73-7.76 (m, 10H, *ortho* C_6H_5); ^{13}C NMR (ppm, C_6D_6) 40.1 $(CH_3)_2SO$, 130.4, 131.5, 132.5, 133.7, 135.1 (C_6H_5)

Attempted synthesis of $[W_2(O)_4(\mu_2\text{-}OSiPh_3)_2(OPPh_3)_2]$ (P4)

A solution of Ph_3SiONa (0.19g, 0.67 mmol) in 15 ml of THF was added dropwise to an ice cold, stirred solution of $[W(O)_2Cl_2(OPPh_3)_2]$ (0.25g, 0.30 mmol) in 10 ml of THF. The mixture was stirred overnight whilst it warmed to room temperature yielding a clear solution. The volatiles were evaporated *in vacuo* and the residue extracted with 50 ml of toluene. Solvent was removed from the extract to yield the title product (0.32g, 80%).

Compound (P4) was stable if stored under nitrogen but rapidly decomposed in solution if exposed to moisture.

Analysis (calculated for $C_{72}H_{60}O_8P_2Si_2W_2$) Found C 68.8 (65.3), H 5.16 (4.58) %; IR 1179, 1117, 1071, 1028, 997, 964, 911, 889, 723, 710, 696 cm^{-1}. ^1H NMR (ppm, C_6D_6) 6.9-7.0 (m, 18H, meta, para OPPh_3), 7.1-7.2 (m, 18H, OSiPh_3), 7.5-7.6 (m, 12H, OPPh_3), 7.9-8.0 (m, 12H, OSiPh_3); ^{13}C NMR (ppm, C_6D_6) 128.3, 128.8, 129.0, 130.0, 132.1, 132.9, 136.1, 138.0 (C_6H_5)

Reaction of WCl_6 with $[Ph_2SiO]_3$ (method A)

A schlenk tube was charged with WCl_6 (0.2g, 0.50 mmol), $[Ph_2SiO]_3$ (0.91g, 1.53 mmol), 25 ml of THF, and the mixture stirred at room temperature. An immediate reaction ensued, the dark brown suspension becoming orange and fading to a green colour over the next 2 hours. Stirring was continued overnight to yield a viscous blue solution, at which stage the volatiles were removed *in vacuo* to yield a viscous blue oil. The oil was redissolved in 25 ml of toluene, stored at -30°C overnight and the resulting solid decanted from the oil. The solid was washed with 20 ml of a cold 1:1 hexane-dichloromethane mixture to yield unreacted cyclotrisiloxane (0.73g, 1.23 mmol). The washings were combined with the blue oil and the volatiles removed *in vacuo*. The oil was redissolved in 25 ml of acetone and sufficient H_2O_2 (20 vol) added dropwise to ensure the blue colouration had disappeared.

Storing at -30°C for 7 days precipitated a white solid which became a sticky residue on filtration at room temperature. Analysis of this compound showed that a ring-opened THF polymer (P5) containing no tungsten had been formed.

Analysis (calculated for $[C_4H_8O]_n$) Found C 66.7 (66.6), H 11.2 (11.20) %; IR 2797, 1484, 1456, 1447, 1298, 1275, 1242, 1210, 1113, 1034, 1015, 984, 963 cm^{-1}; ^1H NMR (ppm, $CDCl_3$) 1.63 (q, 4H, $OCH_2CH_2CH_2CH_2O$), 3.47 (t, 4H, $OCH_2CH_2CH_2CH_2O$); ^{13}C NMR (ppm, $CDCl_3$) 26.5 ($OCH_2CH_2CH_2CH_2O$), 34.1 ($OCH_2CH_2CH_2CH_2O$)

Reaction of WCl_6 with $[Ph_2SiO]_3$ (method B)

A schlenk tube was charged with WCl_6 (0.31g, 0.78 mmol) and $[Ph_2SiO]_3$ (0.47g, 0.78 mmol), 30 ml of dichloromethane, and the mixture stirred at room temperature. The initial green color of the suspension faded to give a dark orange solution after 5 minutes. Stirring was continued for a further hour and then the solution was concentrated to a third of the original volume. The solid formed on standing was decanted from the supernatant liquor, washed with cold dichloromethane (2 × 10 ml) and dried in vacuo. Yield (0.17g, 64%) of $[W(O)Cl_4]$.

IR 960, 890, 867, 808, 779, 670, 391, 355, 322, 300 cm^{-1}

The washings were combined with the supernatant liquor and the volatiles removed to yield an orange solid which decomposed to yield a sticky off-white residue. Washing the residue with 40 ml of toluene yielded a colourless filtrate and a fine white powder which contained no siloxane. The extract was concentrated to 10 ml and stored at 0°C for 10 days to yield unreacted hexaphenylcyclotrisiloxane (0.34g, 0.57 mmol).

Reaction of WCl_6 with $[Ph_2SiO]_3$ (method C)

A schlenk tube was charged with WCl_6 (0.34g, 0.86 mmol), $[Ph_2SiO]_3$ (0.51g, 0.86 mmol) and 50 ml of acetonitrile. The resulting mixture containing a brown suspension was stirred at room temperature for 3 days, the solid decanted from the supernatant liquor and washed with cold acetonitrile (2 × 5 ml) to yield unreacted cyclosiloxane (0.32g, 0.54 mmol). Evaporation of the filtrate *in vacuo* yielded a sticky orange solid which was washed with toluene (2 × 15 ml) and cautiously dried *in vacuo* to yield $[W(O)Cl_4]$ (0.24g, 82%). Evaporation of the toluene washings yielded a white residue which was recrystallised from 1:1 dichloromethane-hexane to give a further batch of pure cyclotrisiloxane (0.12g, 0.20 mmol).

Synthesis of [WO{(OSiPh$_2$OSiPh$_2$OSiPh$_2$O)}$_2$·THF] (P6)

A schlenk tube containing [W(O)Cl$_4$] (1.12g, 3.28 mmol) and [Ph$_2$SiO]$_3$ (3.9g, 6.56 mmol) and 50 ml of THF was stirred at room temperature for 3 days. The resulting viscid blue liquor was concentrated to one third of the original volume, cooled to -30°C for 4 days and filtered to remove unreacted hexaphenylcyclotrisiloxane. The cyclotrisiloxane was freed of the blue oil by washing with a 20 ml portion of cold 2:1 hexane-dichloromethane. The oil and the washings were combined and evaporated to yield a viscous blue oil which was extracted with 30 ml of a 2:1 dichloromethane-hexane mixture. Filtration removed insoluble tungsten oxides, and on cooling the filtrate to 0°C small needles of the product (P7), [WO{(OSiPh$_2$OSiPh$_2$OSiPh$_2$O)}$_2$] incorporating two coordinated THF molecules precipitated (0.92g, 18%).

A second recrystallisation from 2:1 dichloromethane-hexane yielded crystals suitable for a structural determination (0.44g, 9%). The product (P6) was found to be stable in air both in the solid state and in solution.

Analysis (calculated for P7 $C_{80}H_{86}O_{11}Si_6W$) C 61.4 (61.4), H 4.89 (4.90) %; IR 1694, 1591, 1306, 1227, 1123, 1076, 1028, 997, 968, 914, 741, 720, 698 cm^{-1}; ^{1}H NMR (ppm, CDCl$_3$) 1.18 (s, 4H, β-CH$_2$ of THF1), 1.54 (q, 4H, β-CH$_2$ of THF2), 3.34 (t, 4H, α-CH$_2$ of THF1), 3.42 (t, 4H, α-CH$_2$ of THF2), 6.97-7.54 (m, 60H, C$_6$*H*$_5$), ^{13}C NMR (ppm, CDCl$_3$) 23.9 (β-C*H*$_2$ of THF1), 25.5 (β-*C*H$_2$ of THF2), 68.1 (α-*C*H$_2$ of THF1), 69.6 (α-*C*H$_2$ of THF2), 126.5, 126.6, 126.8, 128.9, 129.0, 133.3, 133.4, 133.5, 133.8, 134.0, 134.2 (*C*$_6$*H*$_5$), ^{29}Si NMR (ppm, CDCl$_3$, Cr(acac)$_3$) -21.8, -40.4 (WO*Si*Ph$_2$O), -43.9 (WOSiPh$_2$O*Si*Ph$_2$O).

Analysis (calculated for P6 $C_{76}H_{68}O_{10}Si_6W$) Found C 61.1 (61.1), H 4.66 (4.60) %; IR 1962, 1894, 1825, 1590, 1568, 1428, 1306, 1117, 1076, 1028, 997, 968, 918, 743, 718, 698 cm^{-1}; ^{1}H NMR (ppm, CDCl$_3$) 1.28 (s, 4H, β-C*H*$_2$ of THF), 3.50 (t, 4H, α-C*H*$_2$ of THF), 7.06-7.61 (m, 60H, C$_6$*H*$_5$), ^{13}C NMR (ppm, CDCl$_3$) 24.9 (β-*C*H$_2$ of THF), 69.1 (α-*C*H$_2$ of THF), 127.6, 127.7, 129.9, 130.0, 134.3, 134.4, 134.9, 135.2 (*C*$_6$H$_5$), ^{29}Si NMR (ppm, CDCl$_3$, Cr(acac)$_3$) -40.5 (WO*Si*Ph$_2$O), -44.1 (WOSiPh$_2$O*Si*Ph$_2$O).

Reaction of [W(O)Cl$_4$] with [Ph$_2$SiO]$_4$

A schlenk tube was charged with [W(O)Cl$_4$] (0.22g, 0.64 mmol), [Ph$_2$SiO]$_4$ (1.06g, 1.34 mmol) and 40 ml of THF. The mixture was stirred at room temperature for 1 hour to yield a green suspension. Stirring was continued for a further 3 days resulting in the formation of an intractable, viscous blue oil. The volatiles were removed in vacuo, and toluene (ca 30 ml) added and the mixture stirred for 1 hour. Storage of the filtrate at -30°C for 14 days precipitated colourless platelets. The solvent was decanted and the crystals washed with a cold 2:1 mixture of hexane-dichloromethane to yield pure

$[Ph_2SiO]_4$ (0.73g, 0.96 mmol). The washings were combined with the remaining blue oil, the volatiles removed under vacuum and the oil extracted with 45 ml 2:1 dichloromethane-hexane mixture. Filtration removed insoluble blue tungsten oxides, slow concentration of the solution produced further unreacted cycloterasiloxane (0.22g, 0.32 mmol).

Reaction of $[W(O)_2Cl_2(DMSO)_2]$ with $[Ph_2SiO]_3$

The contents of a schlenk tube containing $[W(O)_2Cl_2(DMSO)_2]$ (0.34g, 0.77 mmol), $[Ph_2SiO]_3$ (0.46g, 0.77 mmol) and 30 ml of THF were stirred at room temperature for 1 day to yield a white suspension. Volatiles were removed *in vacuo* and 30 ml of toluene added to the solid and the suspension stirred for 1 hour. Filtration removed insoluble $[W(O)_2Cl_2(DMSO)_2]$ (0.31g) evaporation of the solvent yielded the toluene soluble products, which contained only unreacted cyclotrisiloxane (0.42g)

Synthesis of $[WO\{OSiPh_2O\}_2]_n$ (P8)

A solution of $Ph_2Si(ONa)_2$ (0.73g, 2.8 mmol) prepared *in situ* was added dropwise to an ice-cold, stirred orange suspension of $[W(O)Cl_4]$ (0.48g, 1.4 mmol) in 20 ml of THF. An immediate reaction ensued producing a slightly blue solution. The mixture was allowed to warm to room temperature overnight and then volatiles were removed *in vacuo*. Extraction with 50 ml of toluene followed by removal of the solvent yielded the title product (P8) (0.65g, 77%).

Compound (P8) was stable but hygroscopic on exposure to air although it demonstrated greater stability in solution than the monodentate siloxides. The microanalysis below indicates a monohydrated form.

Analysis (calculated for $C_{24}H_{22}O_6Si_2W$) Found C 44.6 (44.6), H 3.75 (3.44) %; IR 1591, 1429, 1306, 1119, 1055, 1026, 997, 961, 916, 775, 741, 720, 700, 660 cm^{-1}. ^1H NMR (ppm, CD_2Cl_2) 7.0-7.15 (8H, m, *meta* C_6H_5), 7.2-7.3 (4H, m, *para* C_6H_5), 7.4-7.6 (4H, m, *ortho* C_6H_5), ^{13}C NMR (ppm, CD_2Cl_2) 127.9, 130.1, 134.7, 135.0, 135.4, 135.7 (C_6H_5)

Fine needles unsuitable for a structural determination, were produced on recrystallisation from THF, toluene or dichloromethane solutions.

Attempted synthesis of $[WO\{O(SiPh_2O)_3\}_2 \cdot THF]$ (P9)

A solution of $[Ph_2(OH)Si]_2O$ (1.94g, 4.68 mmol) was added with stirring to an ice cold schlenk tube charged with freshly cleaned sodium (0.27g, 11.74 mmol) suspended in 15 ml of THF. The mixture was stirred overnight at room temperature and the unreacted sodium removed by filtration. The filtrate was added dropwise to an ice cold suspension of $[W(O)Cl_4]$ (0.85g, 2.29 mmol) in 15 ml of THF and stirred at room temperature overnight to give a pale blue suspension. The volatiles were

removed *in vacuo* and the solid extracted with 80 ml of toluene. The solvent was decanted and evaporated to half volume, upon cooling in a freezer white needles were precipitated. Filtration, washing with pentane (2 × 10 ml) and drying under vacuum gave a white solid (2.18g).

Analysis (calculated for $C_{76}H_{68}O_{10}Si_6W$) Found C 50.2 (61.1), H 4.27 (4.6) %; IR 1591, 1429, 1306, 1119, 1123, 1063, 1028, 997, 961, 920, 775, 743, 720, 698; ^{1}H NMR (ppm, $CDCl_3$) 2.3 (s, β-C*H*$_2$ of THF), 3.7 (s, α-C*H*$_2$ of THF), 7.12-7.23 (m, C_6H_5), 7.30-7.37 (m, C_6H_5), 7.52-7.55 (m, C_6H_5), 7.69-7.12 (m, C_6H_5); ^{13}C NMR (ppm, $CDCl_3$) 25.3 (β-*C*H$_2$ of THF), 69.9 (α-*C*H$_2$ of THF), 128.4, 129.2, 130.1, 134.7, 135.0, 135.7 (*C*$_6$H$_5$)

Reaction of $K_4Mo_2Cl_8$ with $Ph_2Si(OH)_2$ (method 1) (P10)

To a mixture of $K_4[Mo_2Cl_8]$ (0.3g, 0.48 mmol) in 30 ml of freshly distilled toluene was added of diphenylsilanediol (0.41g, 1.9 mmol) in 30 ml of toluene. The dark red suspension was stirred under nitrogen for 48 hours until the initial colour became slightly pink. Filtering the suspension through a Buchner funnel yielded a pink solid (0.63g) which was washed with small portions of toluene and then cold light petroleum.

Analysis (Calculated for $C_{48}H_{40}O_8Si_4K_4Mo_2$). Found C 40.3 (47.8), H 3.4 (3.3); IR 3168, 1429, 1130, 1121, 909, 882, 837, 740, 721, 698, 509, 482, 463 cm^{-1}.

Reaction of $K_4Mo_2Cl_8$ with $Ph_2Si(OH)_2$ (method 2) (P11)

To $K_4[Mo_2Cl_8]$ (0.2g, 0.31 mmol) in 25 ml of toluene was added diphenylsilanediol (0.27g, 1.24 mmol) in 60 ml of toluene. The mixture was stirred under nitrogen for 192 hours before the dark red solution was filtered to yield a pink solid (0.2g).

Analysis (Calculated for $C_{48}H_{40}O_8Si_4K_4Mo_2$). Found C 17.2 (47.8), H 1.60 (3.3); IR 3200, 1591, 1429, 1130, 1121, 1047, 1028, 997, 882, 837, 741, 721, 698, 532, 482, 463 cm^{-1}.

Reaction of $K_4Mo_2Cl_8$ with $Ph_2Si(OH)_2$ with NEt_3 (P12)

To a suspension of $K_4[Mo_2Cl_8]$ (0.23g, 0.34 mmol) in 10 ml of THF was added of diphenyl-silanediol (0.28g, 1.3 mmol) in 40 ml of THF. The mixture was stirred under nitrogen and excess triethylamine added using a Pasteur pipette before being left to stir for 91 hours. Filtering under a constant stream of nitrogen yielded a pink solid (0.12g).

Analysis (Calculated for $C_{48}H_{40}O_8K_4Mo_2Si_4$). Found C 3.37 (47.8), H 0.9 (3.3); IR 1157, 1069, 976.

Reaction of $K_4Mo_2Cl_8$ with $[Me_2Si(ONa)]_2O{\cdot}5H_2O$ (method 1) (P13)

To $K_4[Mo_2Cl_8]$ (0.2g, 0.31 mmol)was added tetramethyldisiloxane-1,3-diol disodium salt (0.39g, 1.31 mmol) in 50 ml of THF. The red suspension was stirred under nitrogen for 96 hours before being filtered under a constant stream of nitrogen. Washing with a small portion of THF yielded 0.34g of a red/pink solid.

Analysis (Calculated for $C_{16}H_{48}O_{12}K_4Mo_2Si_8$). Found C 6.6 (12.4), H 0.75 (3.1); IR 3384, 1156, 1048, 945, 882, 843 cm^{-1}.

Reaction of $K_4Mo_2Cl_8$ with $[Me_2Si(ONa)]_2O{\cdot}5H_2O$ (method 2) (P14)

To $K_4[Mo_2Cl_8]$ (0.2g, 0.34 mmol) in 20 ml of THF was added tetramethyldisiloxane-1,3-diol, disodium salt (0.4g, 1.4 mmol). The mixture was stirred under nitrogen for 192 hours and the brown solid formed filtered and washed with THF to yield 0.4g of product.

Analysis (Calculated for $C_{16}H_{48}O_{12}K_4Mo_2Si_8$). Found C 4.5 (12.4), H 1.0 (3.1); IR 3308, 1730, 1674, 1554, 1262, 1156, 1053, 1022, 857, 835, 820, 721, 702, 677, 640, 550, 475 cm^{-1}.

Reaction of $K_4Mo_2Cl_8$ and Ph_3SiOH (P15)

To $K_4[Mo_2Cl_8]$ (0.2g, 0.31 mmol) was added triphenylsilanol (0.69g, 2.5 mmol) in 50 ml of THF. The dark red suspension was stirred at room temperature under nitrogen for 96 hours before being filtered under a constant stream of nitrogen. Washing with a small portion of THF (sieve dried) yielded 0.2g of pink solid.

Analysis (Calculated for $C_{154}H_{120}O_8K_4Mo_2Si_8$). Found C 0.3 (67.8), H 0.2 (4.7); No bands 4000-400 cm^{-1}.

Reaction of $K_4Mo_2Cl_8$ with triphenylsilanol and triethylamine (P16)

To $K_4[Mo_2Cl_8]$ (0.14g, 0.21 mmol) in 10 ml of THF was added 0.49g (1.78 mmol) of triphenylsilanol in 35 ml of THF. The mixture was stirred under nitrogen and excess triethylamine added and then left stirring for 190 hours after which the solid was filtered under a constant stream of nitrogen to yield a brown solid (0.27g) which was washed with two portions of sieve dried THF.

Analysis (Calculated for $C_{154}H_{120}O_8K_4Mo_2Si_8$). Found C 22.0 (67.8), H 4.7 (5.6), N 4.11 (0.0). IR Nujol mull unobtainable.

6.4.3 CROWN ETHER-SILANOL COMPLEXES

The Preparation of 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (1-Aza-18-crown-6) (C1)

A 500 ml, 3 neck round bottomed flask was flame dried and a solution of diethanolamine (9.46g, 90.0 mmol) in 300 ml of ^{t}BuOH added. Freshly cleaned potassium metal (CARE) (4.0g, 102.0 mmol) was dissolved with vigorous stirring and the mixture warmed to 40°C. A solution of tetraethyleneglycol-*p*-ditosylate (22.5g, 44.7 mmol) in 100 ml of THF was added dropwise over a period of 2 hours and the resultant pinkish suspension allowed to stir overnight. Filtration at the pump yielded a slightly pink solution and a white residue which was washed with dichloromethane (3 × 30 ml) and the extracts combined with the filtrate. Volatiles were removed under vacuum and the residue suspended in 25 ml of distilled water. The suspension was extracted with hexane (2 × 30 ml) and the organic phase discarded. Extraction of the aqueous phase with dichloromethane (5 × 30 ml) and removal of the volatiles *in vacuo* yielded a slightly reddish residue which was readily purified by vaccum distillation on a Kugelrohr apparatus (125°C, @ 0.1 mmHg). The colourless oil so obtained rapidly solidified on standing at room temperature to yield the title compound (**C1**) as an oily white solid (8.36g, 71%).

Analysis (calculated for $C_{12}H_{25}O_5N$) Found C 54.6 (54.7), H 9.33 (9.58), N 5.20 (5.35) %; IR 3196, 1636, 1476, 1350, 1331, 1250, 1211, 1120, 1013, 955, 887, 843, 781, 681 cm^{-1}; ^{1}H NMR (ppm, $CDCl_3$) 2.00 (br s, 1H, $CH_2N\mathit{H}CH_2$), 2.79 (t, 4H, $HNC\mathit{H}_2CH_2O$), 3.60-3.69 (m, 20H, $C\mathit{H}_2OC\mathit{H}_2$), ^{13}C NMR (ppm, $CDCl_3$) 49.6 ($\mathit{C}H_2HNC\mathit{H}_2$), 70.3, 71.5 ($\mathit{C}H_2OC\mathit{H}_2$)

Preparation of 1,4,10,13-tetraoxo-7,16-diazacyclooctadecane (C2)

A solution of 2,2'-(ethylenedioxy)bis(ethylamine) (7.4g, 50.0 mmol) in 100 ml of MeCN was added dropwise over 2 hours to a boiling solution of triethylene glycol di-*p*-tosylate (20.0g, 43.0 mmol) and finely ground sodium carbonate (26.5g, 250.0 mmol) in 400 ml of acetonitrile. The mixture was allowed to reflux for a further 18 hours and then allowed to cool to room temperature. The resulting suspension was filtered and the solvent removed from the filtrate to yield a residue which was extracted in a boiling mixture of 100 ml of 1:1 dioxane and acetone. The solution was stored at -30°C overnight and the white solid precipiated decanted from the solvent. The solid was dissolved in water and the aqueous solution extracted with chloroform (6 × 20 ml). The chloroform was removed *in vacuo* and the solid recrystallised from heptane to yield the title product (**C2**) as a white powder (1.0g, 10%, mpt 109-111°C).

Analysis calc. for ($C_{20}H_{26}N_2O_4$) Found C 54.8 (54.9), H 10.1 (9.9), N 10.6 (10.7) %; IR 3320, 1138 cm^{-1}; ^{1}H NMR (ppm, $CDCl_3$) 2.22 (s, 2H, $CH_2CH_2N\mathit{H}CH_2CH_2$), 2.80 (8H, t, $CH_2C\mathit{H}_2NHC\mathit{H}_2CH_2$,

J = 4.2 Hz), 3.61 (16H, m, $CH_2CH_2OCH_2CH_2$); ^{13}C NMR (ppm, $CDCl_3$) 49.2 ($CH_2CH_2NHCH_2CH_2$), 70.1, 70.3 ($CH_2CH_2OCH_2CH_2$); m/e (C.I.) 325.1 $(M+H+C_4H_{10})^+$, 305.3 $(M+H+C_3H_6)^+$, 263.2 $(M+H)^+$, 132.1 $(M+H-C_6H_{13}NO_2)^+$

Synthesis of $(Ph_3SiOH)\cdot$18-crown-6 (C3) and $(Ph_3SiOH)_2\cdot$18-crown-6$\cdot(H_2O)_2$ (C4)

A 100 ml round bottomed flask containing 18-crown-6 (0.32g, 1.21 mmol), Ph_3SiOH (1.00g, 3.63 mmol) and 25 ml of toluene was heated under reflux for 2 hours and then allowed to cool to room temperature. Concentration of the solution to half the original volume and cooling to 0°C for 4 days precipitated unreacted silanol which was removed by filtration. The volume of the filtrate was further reduced, and the solution cooled to -30°C for 7 days to yield the title compound (C3) as tiny transparent crystals which were decanted and washed with 60-80° petroleum ether (2 × 10 ml) (0.57g, 39%).

The filtrate was further reduced in volume and petroleum ether (60-80) added so as to form a layer. Storage at -30°C for 7 months precipitated crystals of $(Ph_3SiOH)\cdot$18-crown-6$\cdot(H_2O)_2$ (C4) (0.15g, 15%).

Attempts at recrystallising (C3) from the minimum volume of warm toluene yielded transparent crystals of (C4) which were found to be suitable for a structural determination.

Compound (C3) also proved to be hygroscopic in the solid state and exposure to air over a period of 7 months resulted in the coordination of 2 molecules of water to yield $(Ph_3SiOH)_3\cdot$18-crown-6$\cdot(H_2O)_2$ (C5).

Compound (C3) analysis (calculated for $C_{66}H_{72}O_9Si_3$) Found C 72.6 (72.5), H 6.65 (6.66) %; IR 3200, 1960, 1889, 1428, 1350, 1250, 1117, 1026, 997, 961, 901, 855, 841, 741, 711, 698 cm^{-1}; ^1H NMR (ppm, $CDCl_3$) 3.2 (s, 3H, SiO*H*), 3.6 (24H, s, OCH_2CH_2O), 7.35 (m, 27H, *meta, para* C_6H_5), 7.60 (m, 18H, *ortho* C_6H_5), ^{13}C NMR (ppm, $CDCl_3$) 70.5 (OCH_2CH_2O), 127.7 (*meta* C_6H_5), 129.9 (*para* C_6H_5), 134.9 (*ortho* C_6H_5), 135.8 (*ipso* C_6H_5),^{29}Si NMR (ppm, $CDCl_3$, $Cr(acac)_3$) -13.4.

Compound (C4) analysis (calculated for $C_{48}H_{60}O_{10}Si_2$) Found C 67.7 (67.5), H 7.16 (7.01) %; IR 3549, 3508, 3206, 3042, 2743, 1630, 1466, 1426, 1350, 1285, 1250, 1111, 1063, 1030, 997, 961, 901, 841, 743, 712 cm^{-1}; ^1H NMR (ppm, $CDCl_3$) 2.35 (s, 4H, H_2O), 3.65 (s, 24H, OCH_2CH_2O), 7.25-7.46 (m, 18H, *meta, para* C_6H_5), 7.61-7.64 (m, 12H, *ortho* C_6H_5); ^{13}C NMR (ppm, $CDCl_3$) 70.3 (OCH_2CH_2O), 127.7 (*meta* C_6H_5), 129.9 (*para* C_6H_5), 134.9 (*ortho* C_6H_5), 135.3 (*ipso* C_6H_5), ^{29}Si NMR ($CDCl_3$, $Cr(acac)_3$) -13.0.

Compound (C5) analysis (calculated for $C_{66}H_{76}O_{11}Si_3$), Found C 70.1 (70.2) , H 6.67 (6.79) %; IR 3550, 3501, 3216, 3065, 3044, 3009, 1466, 145, 1426, 1350, 1132, 1111, 961, 901, 841, 743, 712 cm^{-1}.

Synthesis of $(Ph_3SiOH)_2$·1-aza-18-crown-6·H_2O (C6) (method A)

A 100 ml round bottomed flask containing monoazacrown (0.28g, 1.06 mmol), Ph_3SiOH (0.29g, 1.05 mmol) and 35 ml of toluene was heated under reflux for 3 hours. The resulting solution was cooled to room temperature, concentrated to 15 ml and stored at 0°C for 2 days to deposit a white solid of unreacted silanol. The filtrate was further reduced to 10 ml and 5ml of 60-80° petroleum ether added. Storage at -30°C for 7 days yielded small crystals which were filtered, washed with petroleum ether (2 x 10 ml), and air dried to give the title compound (0.57g, 53%). Hydrated crystals suitable for x-ray crystallography were obtained from slow concentration of a toluene solution.

Analysis (calculated for $C_{48}H_{59}NO_8Si_2$) Found C 68.8 (69.1), H 7.25 (7.14), N 1.75 (1.69) %; IR 3523, 3453, 3135, 1428, 1350, 1345, 1256, 1246, 1113, 961, 947, 901, 889, 847, 833, 745, 710 cm^{-1}; ^1H NMR (ppm, $CDCl_3$) 2.58 (t, 4H, $HNC\boldsymbol{H}_2CH_2O$), 3.46 (q, 8H, $HNCH_2C\boldsymbol{H}_2OC\boldsymbol{H}_2CH_2O$), 3.55 (m, 12H, $HNCH_2CH_2OCH_2C\boldsymbol{H}_2OC\boldsymbol{H}_2C\boldsymbol{H}_2O$), 3.9 (bs, 2H, $\boldsymbol{H}_2O$) 7.23-7.42 (m, 20H, *meta, para* $C_6\boldsymbol{H}_5$), 7.60-7.64 (m, 10H, *ortho* $C_6\boldsymbol{H}_5$); ^{13}C NMR (ppm, $CDCl_3$) 48.6 ($NHCH_2CH_2$), 69.5 ($NHCH_2CH_2OCH2$), 69.9 ($HNCH_2CH_2OCH_2CH_2O$), 70.2 ($HNCH_2CH_2OCH_2CH_2O$), 127.6, 129.6, 134.9, 135.9 (C_6H_5)

Synthesis of (Ph_3SiOH)·1-aza-18-crown-6·H_2O (C6) (method B)

A 100 ml round bottomed flask charged with monoazacrown (0.25g, 0.95 mmol), Ph_3SiOH (0.78g, 2.85 mmol), and 50 ml of toluene was heated under reflux for 4 hours and then cooled to room temperature. The volume of solvent was reduced to 15 ml and the solution stored at 0°C for 12 days to precipitate tiny crystals. Filtration removed (0.22g, 0.80 mmol) of unreacted Ph_3SiOH, the filtrate was treated with equal volume of petroleum ether (60-80°) and returned to the refridgerator. Small crystals were obtained after 14 days, washing with petroleum ether (2 x 10 ml), and air drying gave the title compound (0.48g, 61%).

Analysis (calculated for $C_{48}H_{59}NO_8Si_2$) Found C 69.2 (69.1), H 7.16 (7.14), N 1.69 (1.69) %; IR 3524, 3455, 3252, 3135, 1428, 1350, 1256, 1246, 1113, 961, 947, 901, 891, 847, 833, 745, 710 cm^{-1}; ^1H NMR (ppm, $CDCl_3$) 2.73 (t, 4H, $HNC\boldsymbol{H}_2CH_2O$), 3.57 (q, 8H, $HNCH_2C\boldsymbol{H}_2OC\boldsymbol{H}_2CH_2O$), 3.62 (m, 12H, $HNCH_2CH_2OCH_2C\boldsymbol{H}_2OC\boldsymbol{H}_2C\boldsymbol{H}_2O$), 7.26-7.47 (m, 20H, *meta, para* $C_6\boldsymbol{H}_5$), 7.62-7.65 (m, 10H, *ortho* $C_6\boldsymbol{H}_5$); ^{13}C NMR

(ppm, $CDCl_3$) 48.4 ($NHCH_2CH_2$), 69.9 ($NHCH_2CH_2OCH2$), 70.4 ($HNCH_2CH_2OCH_2CH_2O$), 70.7 ($HNCH_2CH_2OCH_2CH_2O$), 127.4, 129.7, 135.3, 135.6 (C_6H_5)

Synthesis of $(Ph_3SiOH)_2$·7,16-diaza-18-crown-6 (C7) (method A)

A 50 ml round bottomed flask containg diazacrown (0.06g, 0.23 mmol), Ph_3SiOH (0.13g, 0.46 mmol) and 20 ml of touene was heated under reflux for 2 hours. The solution was concentrated to half the original volume and stored at 0°C for 2 days yielding large colourless crystals. Filtration of the solid, washing with 60-80 petroleum ether (2 x 5 ml) and air drying yielded crystals (0.1g, 58%) in a form suitable for a structural determination.

Analysis (calculated for $C_{48}H_{58}N_2O_6Si_2$) Found C 70.8 (70.8), H 7.16 (7.12), N 3.36 (3.44) %; IR 3308, 1428, 1350, 1291, 1252, 1109, 1069, 992, 909, 891, 845, 741, 698 cm^{-1}; ^1H NMR (ppm, $CDCl_3$) 2.68 (t, 8H, $HNCH_2CH_2O$), 3.48 (m, 16H, $HNCH_2CH_2O$), 7.25-7.42 (m, 20H, *meta, para* C_6H_5), 7.61-7.65 (m, 10H, *ortho* C_6H_5); ^{13}C NMR (ppm, $CDCl_3$)49.1 ($HNCH_2CH_2O$), 70.2 ($HNCH_2CH_2O$), 127.9, 130.0, 135.1, 136.0 (C_6H_5), ^{29}Si NMR (ppm, $CDCl_3$, $Cr(acac)_3$) -16.0.

Synthesis of $(Ph_3SiOH)_2$·7,16-diaza-18-crown-6 (C7) (method B)

A mixture of diazacrown (0.22g, 0.84 mmol), Ph_3SiOH (0.72g, 2.60 mmol) and 25 ml of toluene heated under reflux for 3 hours. Storing at 0°C for 3 days precipitated one equivalent of Ph_3SiOH. Removal of this solid and further concentration of the filtrate to 10 ml yielded colourless cystals after storage at 0°C for 7 days. The crystals were filtered, washed with pentane (2 × 5 ml) and air dried to yield the title product (0.35g, 52%).

Analysis (calculated for $C_{48}H_{58}N_2O_6Si_2$) Found C 71.0 (70.8), H 7.25 (7.12), N 3.40 (3.44) %; IR 3308, 1958, 1456, 1350, 1291, 1252, 1109, 1069, 992, 891, 845, 741, 710, 698 cm^{-1}; ^1H NMR (ppm, $CDCl_3$) 2.69 (t, 8H, $HNCH_2CH_2$), 3.49 (m, 16H, CH_2CH_2O), 7.25-7.42 (m, 20H, *meta, para* C_6H_5), 7.61-7.65 (m, 10H, *ortho* C_6H_5); ^{13}C NMR (ppm, $CDCl_3$) 49.0 ($HNCH_2CH_2O$), 70.0 ($HNCH_2CH_2O$), 127.8, 129.9, 135.0, 135.8 (C_6H_5).

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Appendices

APPENDIX 1: NOTES ON [WO{O(Ph$_2$SiO)$_3$}$_2$·THF] (P6)

A crystal of approximate dimensions 0.2 x 0.2 x 0.3 mm was used for data collection.

Crystal data: $C_{76}H_{68}O_{10}Si_6W$, M = 1493.69, Triclinic , a = 9.915(5), b = 13.865(3), c = 25.712(6) Å , α = 82.47(2), β = 83.83(3), γ = 87.76(3)°, U = 3482.8(21) Å^3, space group P-1(No.2), Z = 2, D_c = 1.424 g cm^{-3}, (mMo-K_a) = 1.820 mm^{-1}, F(000) = 1524. Crystallographic measurements were made at 293(2)° K on a CAD4 automatic four-circle diffractometer in the range 2.04<q<22.00°. Data (8582 reflections) were corrected for Lorentz and polarization and also for absorption.[1] (Max. and Min absorption corrections; 1.00, 0.608 respectively).

In the final least squares cycles all atoms except for carbons 73-76 were allowed to vibrate anisotropically. In addition, phenyl groups were treated as rigid hexagons and the distances in the coordinated solvent were restrained to ideal values. Hydrogen atoms were included at calculated positions where relevant.

The solution of the structure (SHELX86)[2] and refinement (SHELX93)[3] converged to a conventional [i.e. based on 5864 with Fo>4s(Fo)] $R1$ = 0.0573 and $wR2$ = 0.1436. Goodness of fit = 1.084. The max. and min. residual densities were 1.431 and -1.099eÅ^{-3} respectively. The asymmetric unit (shown in figure 42), along with the labelling scheme used was produced using ORTEX.[4] Final fractional atomic co-ordinates and isotropic thermal parameters, bond distances and angles are given in Tables 50, 51 and 52 respectively. Tables of anisotropic temperature factors are available as supplementary data.

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Table 49. Crystal data and structure refinement for (P6).

Empirical formula	C_{76} H_{68} O_{10} Si_6 W
Formula weight	1493.69
Temperature	293(2)° K
Wavelength	0.70930 Å
Crystal system	Triclinic
Space group	P-1(No.2)
Unit cell dimensions	a = 9.915(5)Å α= 82.47(2)°
	b = 13.865(3)Å β= 83.83(3)°
	c = 25.712(6)Å γ= 87.76(3)°
Volume	3483(2) Å^3
Z	2
Density (calculated)	1.424 Mg m^{-3}
Absorption coefficient	1.820 mm^{-1}
F(000)	1524
Crystal size	0.2 x 0.2 x 0.3 mm
Theta range for data collection	2.04 to 22.00 °
Index ranges	-11<=h<=11; -15<=k<=15; 0<=l<=29
Reflections collected	8582
Independent reflections	8582 [R(int) = 0.0000]
Min. and max. transmission	0.608 and 1.00
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7526 / 5 / 674
Goodness-of-fit on F2	1.084
Final R indices [I>2σ(I)]	R1 = 0.0573 wR2 = 0.1436
R indices (all data)	R1 = 0.1161 wR2 = 0.2772
Largest diff. peak and hole	1.431 and -1.099 eÅ^{-3}
Weighting scheme	calc $w=1/[\sigma^2(Fo^2)+(0.0884P)^2+12.1634P]$ where $P=(Fo^2+2Fc^2)/3$

Table 50. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for (P6). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
W(1)	117(1)	2411(1)	2476(1)	44(1)
Si(1)	224(4)	2750(2)	3783(1)	52(1)
Si(2)	1283(4)	4908(2)	3514(1)	53(1)
Si(3)	553(4)	4905(2)	2341(1)	50(1)
Si(4)	234(4)	2114(2)	1183(1)	54(1)
Si(5)	-824(4)	-51(2)	1466(1)	53(1)
Si(6)	-88(4)	-76(2)	2639(1)	52(1)
O(1)	340(9)	3743(5)	2344(3)	64(2)
O(2)	1027(9)	5134(5)	2898(3)	65(2)
O(3)	942(9)	3780(5)	3727(3)	60(2)
O(4)	35(10)	2476(5)	3201(3)	72(3)
O(5)	652(11)	2342(5)	1751(3)	78(3)
O(6)	-446(9)	1062(5)	1249(3)	69(2)
O(7)	-456(9)	-304(5)	2075(3)	68(2)
O(8)	305(10)	1043(5)	2636(3)	68(2)
O(9)	2451(10)	2329(6)	2516(4)	84(3)
O(10)	-1564(13)	2446(6)	2444(3)	101(4)
C(1)	1329(9)	1799(5)	4124(3)	56(3)
C(2)	2657(9)	1970(5)	4206(4)	85(4)
C(3)	3434(8)	1234(8)	4459(4)	112(6)
C(4)	2883(10)	327(6)	4631(4)	99(5)
C(5)	1555(11)	156(5)	4550(3)	75(4)
C(6)	778(8)	891(6)	4296(3)	70(4)
C(7)	-1494(7)	2791(6)	4158(3)	56(3)
C(8)	-1649(9)	2646(6)	4706(3)	75(4)
C(9)	-2929(12)	2730(7)	4978(3)	87(4)
C(10)	-4054(8)	2958(7)	4702(5)	115(7)
C(11)	-3899(8)	3103(7)	4154(5)	104(6)
C(12)	-2620(10)	3019(6)	3882(3)	82(4)
C(13)	177(8)	5728(5)	3913(3)	51(3)
C(14)	-786(9)	5358(5)	4316(3)	78(4)
C(15)	-1537(9)	5984(7)	4622(3)	96(5)
C(16)	-1326(9)	6980(7)	4526(3)	84(5)
C(17)	-363(10)	7349(4)	4124(4)	83(5)
C(18)	389(9)	6723(5)	3817(3)	73(4)
C(19)	3119(7)	5145(5)	3561(3)	51(3)
C(20)	3494(9)	5372(6)	4035(3)	70(4)
C(21)	4839(11)	5568(7)	4079(4)	94(5)
C(22)	5808(7)	5536(7)	3648(5)	101(5)

C(23)	5432(9)	5309(7)	3174(4)	92(5)
C(24)	4088(10)	5113(6)	3130(3)	74(4)
C(25)	-1070(8)	5609(6)	2227(3)	57(3)
C(26)	-1867(10)	5314(7)	1867(4)	113(7)
C(27)	-2988(10)	5879(9)	1721(4)	130(8)
C(28)	-3313(9)	6737(8)	1937(5)	106(6)
C(29)	-2516(11)	7031(5)	2298(4)	93(5)
C(30)	-1395(10)	6467(6)	2443(4)	76(4)
C(31)	1895(8)	5246(6)	1791(3)	53(3)
C(32)	2522(10)	6138(5)	1739(4)	76(4)
C(33)	3455(9)	6408(6)	1306(4)	94(5)
C(34)	3762(9)	5786(9)	925(4)	97(5)
C(35)	3135(11)	4894(8)	977(3)	111(6)
C(36)	2202(10)	4624(5)	1410(4)	84(4)
C(37)	-1014(8)	3059(5)	940(3)	50(3)
C(38)	-2391(9)	2865(6)	1024(4)	93(5)
C(39)	-3337(7)	3567(9)	850(5)	114(6)
C(40)	-2906(11)	4463(8)	591(4)	111(6)
C(41)	-1530(12)	4657(5)	506(4)	90(5)
C(42)	-584(8)	3955(6)	681(3)	71(4)
C(43)	1836(9)	2130(6)	737(3)	58(3)
C(44)	1805(10)	2379(7)	197(3)	76(4)
C(45)	3003(14)	2388(8)	-138(3)	117(6)
C(46)	4231(10)	2149(8)	66(6)	126(8)
C(47)	4263(9)	1899(8)	607(7)	135(9)
C(48)	3065(13)	1890(7)	942(4)	95(5)
C(49)	174(8)	-877(4)	1038(3)	52(3)
C(50)	-73(8)	-1867(5)	1137(3)	67(4)
C(51)	616(9)	-2503(4)	820(4)	73(4)
C(52)	1552(9)	-2149(6)	404(3)	81(4)
C(53)	1800(9)	-1159(7)	305(3)	101(5)
C(54)	1110(9)	-522(4)	622(3)	77(4)
C(55)	-2670(8)	-238(6)	1453(3)	62(3)
C(56)	-3540(11)	-226(7)	1914(3)	84(4)
C(57)	-4917(10)	-375(7)	1911(4)	100(5)
C(58)	-5425(8)	-536(7)	1448(5)	101(6)
C(59)	-4555(11)	-548(7)	987(4)	100(5)
C(60)	-3178(10)	-399(7)	990(3)	79(4)
C(61)	1400(8)	-876(5)	2820(3)	53(3)
C(62)	1985(10)	-719(7)	3269(3)	85(5)
C(63)	3085(11)	-1295(8)	3426(4)	121(7)
C(64)	3600(9)	-2028(7)	3134(4)	91(5)
C(65)	3015(10)	-2186(6)	2686(4)	92(5)
C(66)	1915(9)	-1609(6)	2529(3)	76(4)
C(67)	-1578(8)	-318(6)	3150(3)	55(3)
C(68)	-2128(10)	-1239(5)	3256(4)	78(4)

C(69)	-3186(10)	-1424(6)	3653(4)	87(4)
C(70)	-3692(9)	-689(9)	3945(4)	102(5)
C(71)	-3142(11)	231(8)	3839(4)	123(7)
C(72)	-2084(10)	417(5)	3441(4)	89(5)
C(73)	3345(20)	1484(13)	2703(13)	239(15)
C(74)	4799(24)	1800(19)	2743(12)	210(12)
C(75)	5114(22)	2749(21)	2374(12)	239(15)
C(76)	3594(19)	3024(17)	2375(18)	328(23)

Table 51. Bond lengths [Å] and angles [°] for **(P6)**.

W(1)-O(10)	1.675(13)
W(1)-O(1)	1.851(7)
W(1)-O(4)	1.872(8)
W(1)-O(5)	1.896(8)
W(1)-O(8)	1.894(7)
W(1)-O(9)	2.326(10)
Si(1)-O(3)	1.603(8)
Si(1)-O(4)	1.622(8)
Si(1)-C(7)	1.869(8)
Si(1)-C(1)	1.870(7)
Si(2)-O(3)	1.623(8)
Si(2)-O(2)	1.621(8)
Si(2)-C(13)	1.874(6)
Si(2)-C(19)	1.882(8)
Si(3)-O(2)	1.626(8)
Si(3)-O(1)	1.632(7)
Si(3)-C(31)	1.861(8)
Si(3)-C(25)	1.879(7)
Si(4)-O(6)	1.611(8)
Si(4)-O(5)	1.632(8)
Si(4)-C(43)	1.856(9)
Si(4)-C(37)	1.862(7)
Si(5)-O(6)	1.615(8)
Si(5)-O(7)	1.636(8)
Si(5)-C(55)	1.864(8)
Si(5)-C(49)	1.873(6)
Si(6)-O(8)	1.613(7)
Si(6)-O(7)	1.607(8)
Si(6)-C(61)	1.874(7)
Si(6)-C(67)	1.877(8)
O(9)-C(76)	1.5000(12)
O(9)-C(73)	1.5000(12)
C(1)-C(2)	1.39
C(1)-C(6)	1.39
C(2)-C(3)	1.39
C(3)-C(4)	1.39
C(4)-C(5)	1.39
C(5)-C(6)	1.39
C(7)-C(8)	1.39
C(7)-C(12)	1.39
C(8)-C(9)	1.39
C(9)-C(10)	1.39
C(10)-C(11)	1.39
C(11)-C(12)	1.39

C(13)-C(14)	1.39
C(13)-C(18)	1.39
C(14)-C(15)	1.39
C(15)-C(16)	1.39
C(16)-C(17)	1.39
C(17)-C(18)	1.39
C(19)-C(20)	1.39
C(19)-C(24)	1.39
C(20)-C(21)	1.39
C(21)-C(22)	1.39
C(22)-C(23)	1.39
C(23)-C(24)	1.39
C(25)-C(26)	1.39
C(25)-C(30)	1.39
C(26)-C(27)	1.39
C(27)-C(28)	1.39
C(28)-C(29)	1.39
C(29)-C(30)	1.39
C(31)-C(32)	1.39
C(31)-C(36)	1.39
C(32)-C(33)	1.39
C(33)-C(34)	1.39
C(34)-C(35)	1.39
C(35)-C(36)	1.39
C(37)-C(38)	1.39
C(37)-C(42)	1.39
C(38)-C(39)	1.39
C(39)-C(40)	1.39
C(40)-C(41)	1.39
C(41)-C(42)	1.39
C(43)-C(44)	1.39
C(43)-C(48)	1.39
C(44)-C(45)	1.39
C(45)-C(46)	1.39
C(46)-C(47)	1.39
C(47)-C(48)	1.39
C(49)-C(50)	1.39
C(49)-C(54)	1.39
C(50)-C(51)	1.39
C(51)-C(52)	1.39
C(52)-C(53)	1.39
C(53)-C(54)	1.39
C(55)-C(56)	1.39
C(55)-C(60)	1.39
C(56)-C(57)	1.39
C(57)-C(58)	1.39

C(58)-C(59)	1.39
C(59)-C(60)	1.39
C(61)-C(62)	1.39
C(61)-C(66)	1.39
C(62)-C(63)	1.39
C(63)-C(64)	1.39
C(64)-C(65)	1.39
C(65)-C(66)	1.39
C(67)-C(68)	1.39
C(67)-C(72)	1.39
C(68)-C(69)	1.39
C(69)-C(70)	1.39
C(70)-C(71)	1.39
C(71)-C(72)	1.39
C(73)-C(74)	1.5401(13)
C(74)-C(75)	1.5399(11)
C(75)-C(76)	1.5400(13)

O(10)-W(1)-O(1)	96.2(4)
O(10)-W(1)-O(4)	96.3(4)
O(1)-W(1)-O(4)	89.9(3)
O(10)-W(1)-O(5)	97.4(4)
O(1)-W(1)-O(5)	88.4(3)
O(4)-W(1)-O(5)	166.3(4)
O(10)-W(1)-O(8)	96.6(4)
O(1)-W(1)-O(8)	167.1(4)
O(4)-W(1)-O(8)	87.4(3)
O(5)-W(1)-O(8)	91.3(3)
O(10)-W(1)-O(9)	178.8(3)
O(1)-W(1)-O(9)	84.9(3)
O(4)-W(1)-O(9)	84.2(4)
O(5)-W(1)-O(9)	82.1(4)
O(8)-W(1)-O(9)	82.3(3)
O(3)-Si(1)-O(4)	109.5(4)
O(3)-Si(1)-C(7)	111.2(4)
O(4)-Si(1)-C(7)	107.7(5)
O(3)-Si(1)-C(1)	108.8(4)
O(4)-Si(1)-C(1)	109.3(4)
C(7)-Si(1)-C(1)	110.3(4)
O(3)-Si(2)-O(2)	109.4(4)
O(3)-Si(2)-C(13)	109.7(4)
O(2)-Si(2)-C(13)	110.3(4)
O(3)-Si(2)-C(19)	110.6(4)
O(2)-Si(2)-C(19)	107.3(4)
C(13)-Si(2)-C(19)	109.6(4)
O(2)-Si(3)-O(1)	111.3(4)

O(2)-Si(3)-C(31)	110.5(5)
O(1)-Si(3)-C(31)	105.5(4)
O(2)-Si(3)-C(25)	108.3(4)
O(1)-Si(3)-C(25)	110.5(4)
C(31)-Si(3)-C(25)	110.8(4)
O(6)-Si(4)-O(5)	109.9(4)
O(6)-Si(4)-C(43)	110.7(4)
O(5)-Si(4)-C(43)	106.0(5)
O(6)-Si(4)-C(37)	109.0(5)
O(5)-Si(4)-C(37)	109.3(4)
C(43)-Si(4)-C(37)	112.0(4)
O(6)-Si(5)-O(7)	109.4(4)
O(6)-Si(5)-C(55)	110.7(5)
O(7)-Si(5)-C(55)	108.5(5)
O(6)-Si(5)-C(49)	108.9(4)
O(7)-Si(5)-C(49)	110.1(4)
C(55)-Si(5)-C(49)	109.2(4)
O(8)-Si(6)-O(7)	112.7(4)
O(8)-Si(6)-C(61)	108.6(5)
O(7)-Si(6)-C(61)	107.8(4)
O(8)-Si(6)-C(67)	106.9(4)
O(7)-Si(6)-C(67)	110.4(5)
C(61)-Si(6)-C(67)	110.4(4)
Si(3)-O(1)-W(1)	169.8(5)
Si(2)-O(2)-Si(3)	156.2(5)
Si(1)-O(3)-Si(2)	159.3(6)
Si(1)-O(4)-W(1)	165.7(6)
Si(4)-O(5)-W(1)	147.9(7)
Si(4)-O(6)-Si(5)	161.7(6)
Si(6)-O(7)-Si(5)	156.5(5)
Si(6)-O(8)-W(1)	155.9(6)
C(76)-O(9)-C(73)	95(2)
C(76)-O(9)-W(1)	135.7(12)
C(73)-O(9)-W(1)	129.8(11)
C(2)-C(1)-C(6)	120.0
C(2)-C(1)-Si(1)	122.5(5)
C(6)-C(1)-Si(1)	117.5(5)
C(3)-C(2)-C(1)	120.0
C(2)-C(3)-C(4)	120.0
C(3)-C(4)-C(5)	120.0
C(6)-C(5)-C(4)	120.0
C(5)-C(6)-C(1)	120.0
C(8)-C(7)-C(12)	120.0
C(8)-C(7)-Si(1)	120.9(6)
C(12)-C(7)-Si(1)	119.0(6)
C(7)-C(8)-C(9)	120.0

C(10)-C(9)-C(8)	120.0
C(11)-C(10)-C(9)	120.0
C(10)-C(11)-C(12)	120.0
C(11)-C(12)-C(7)	120.0
C(14)-C(13)-C(18)	120.0
C(14)-C(13)-Si(2)	121.6(5)
C(18)-C(13)-Si(2)	118.4(5)
C(13)-C(14)-C(15)	120.0
C(16)-C(15)-C(14)	120.0
C(17)-C(16)-C(15)	120.0
C(16)-C(17)-C(18)	120.0
C(17)-C(18)-C(13)	120.0
C(20)-C(19)-C(24)	120.0
C(20)-C(19)-Si(2)	118.7(5)
C(24)-C(19)-Si(2)	121.3(5)
C(19)-C(20)-C(21)	120.0
C(22)-C(21)-C(20)	120.0
C(23)-C(22)-C(21)	120.0
C(22)-C(23)-C(24)	120.0
C(23)-C(24)-C(19)	120.0
C(26)-C(25)-C(30)	120.0
C(26)-C(25)-Si(3)	117.9(5)
C(30)-C(25)-Si(3)	121.6(5)
C(25)-C(26)-C(27)	120.0
C(28)-C(27)-C(26)	120.0
C(27)-C(28)-C(29)	120.0
C(30)-C(29)-C(28)	120.0
C(29)-C(30)-C(25)	120.0
C(32)-C(31)-C(36)	120.0
C(32)-C(31)-Si(3)	120.8(5)
C(36)-C(31)-Si(3)	119.0(5)
C(33)-C(32)-C(31)	120.0
C(32)-C(33)-C(34)	120.0
C(35)-C(34)-C(33)	120.0
C(34)-C(35)-C(36)	120.0
C(35)-C(36)-C(31)	120.0
C(38)-C(37)-C(42)	120.0
C(38)-C(37)-Si(4)	119.3(5)
C(42)-C(37)-Si(4)	120.7(5)
C(37)-C(38)-C(39)	120.0
C(40)-C(39)-C(38)	120.0
C(39)-C(40)-C(41)	120.0
C(40)-C(41)-C(42)	120.0
C(41)-C(42)-C(37)	120.0
C(44)-C(43)-C(48)	120.0
C(44)-C(43)-Si(4)	119.8(7)

C(48)-C(43)-Si(4)	120.2(7)
C(43)-C(44)-C(45)	120.0
C(46)-C(45)-C(44)	120.0
C(45)-C(46)-C(47)	120.0
C(48)-C(47)-C(46)	120.0
C(47)-C(48)-C(43)	120.0
C(50)-C(49)-C(54)	120.0
C(50)-C(49)-Si(5)	118.1(4)
C(54)-C(49)-Si(5)	121.9(4)
C(49)-C(50)-C(51)	120.0
C(52)-C(51)-C(50)	120.0
C(53)-C(52)-C(51)	120.0
C(52)-C(53)-C(54)	120.0
C(53)-C(54)-C(49)	120.0
C(56)-C(55)-C(60)	120.0
C(56)-C(55)-Si(5)	119.4(6)
C(60)-C(55)-Si(5)	120.6(6)
C(55)-C(56)-C(57)	120.0
C(58)-C(57)-C(56)	120.0
C(57)-C(58)-C(59)	120.0
C(60)-C(59)-C(58)	120.0
C(59)-C(60)-C(55)	120.0
C(62)-C(61)-C(66)	120.0
C(62)-C(61)-Si(6)	117.3(5)
C(66)-C(61)-Si(6)	122.7(5)
C(61)-C(62)-C(63)	120.0
C(62)-C(63)-C(64)	120.0
C(65)-C(64)-C(63)	120.0
C(64)-C(65)-C(66)	120.0
C(65)-C(66)-C(61)	120.0
C(68)-C(67)-C(72)	120.0
C(68)-C(67)-Si(6)	120.4(5)
C(72)-C(67)-Si(6)	119.5(5)
C(67)-C(68)-C(69)	120.0
C(70)-C(69)-C(68)	120.0
C(71)-C(70)-C(69)	120.0
C(70)-C(71)-C(72)	120.0
C(71)-C(72)-C(67)	120.0
O(9)-C(73)-C(74)	112(2)
C(75)-C(74)-C(73)	110(2)
C(74)-C(75)-C(76)	92(2)
O(9)-C(76)-C(75)	125(2)

Table 52. Anisotropic displacement parameters (Å^2 x 10^3) for **(P6)**.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [h^2 a^* 2 U11 + ... + 2 h k a^* b^* U12]$

Atom	U11	U22	U33	U23	U13	U12
W(1)	66(1)	31(1)	36(1)	-6(1)	-16(1)	0(1)
Si(1)	90(2)	38(2)	29(2)	-6(1)	-15(2)	-2(2)
Si(2)	88(2)	36(2)	38(2)	-12(1)	-12(2)	-3(2)
Si(3)	90(2)	30(1)	34(2)	-6(1)	-17(2)	-3(2)
Si(4)	90(3)	39(2)	34(2)	-5(1)	-16(2)	-3(2)
Si(5)	87(2)	41(2)	33(2)	-10(1)	-12(2)	-8(2)
Si(6)	92(2)	32(2)	32(2)	-7(1)	-8(2)	-2(2)
O(1)	122(7)	35(4)	36(5)	0(3)	-17(4)	-12(4)
O(2)	116(7)	42(4)	42(5)	-12(4)	-28(5)	-9(4)
O(3)	101(6)	37(4)	44(5)	-5(3)	-14(4)	-10(4)
O(4)	136(8)	46(4)	37(5)	-5(4)	-19(5)	-4(5)
O(5)	164(9)	46(4)	29(5)	-3(4)	-29(5)	-13(5)
O(6)	120(7)	39(4)	50(5)	-11(4)	-7(5)	-14(4)
O(7)	114(7)	47(4)	47(5)	-15(4)	-13(5)	-4(4)
O(8)	122(7)	34(4)	50(5)	6(3)	-20(5)	-16(4)
O(9)	130(8)	48(5)	80(7)	0(4)	-40(6)	-14(5)
O(10)	206(13)	47(5)	42(6)	5(4)	13(6)	-9(6)
C(1)	90(10)	51(7)	27(7)	-10(5)	-5(6)	12(7)
C(2)	74(10)	72(9)	103(13)	7(8)	-6(9)	-4(8)
C(3)	91(12)	95(12)	155(19)	-23(12)	-35(12)	37(11)
C(4)	120(15)	76(11)	98(13)	-9(9)	-15(11)	35(10)
C(5)	110(12)	59(8)	52(9)	5(6)	-2(8)	-3(8)
C(6)	83(9)	59(8)	64(10)	10(7)	-9(7)	3(7)
C(7)	77(9)	31(5)	68(9)	-12(6)	-35(7)	-2(6)
C(8)	78(10)	83(9)	65(10)	-19(8)	-4(8)	2(8)
C(9)	110(13)	81(10)	71(11)	-26(8)	2(10)	-6(9)
C(10)	89(13)	115(14)	150(20)	-60(14)	-9(13)	9(10)
C(11)	70(11)	85(11)	162(19)	-33(12)	-29(12)	13(9)
C(12)	95(11)	70(9)	85(11)	-18(8)	-28(9)	10(8)
C(13)	69(8)	53(7)	37(8)	-18(6)	-15(6)	-1(6)
C(14)	94(11)	69(9)	76(11)	-26(8)	-8(9)	2(8)
C(15)	123(13)	105(12)	56(10)	-22(9)	12(9)	11(10)
C(16)	108(12)	95(11)	62(10)	-45(9)	-31(9)	40(10)
C(17)	128(13)	48(7)	73(11)	-17(7)	2(9)	10(8)
C(18)	117(11)	51(7)	56(9)	-21(7)	-12(8)	7(8)
C(19)	68(8)	30(5)	52(8)	-3(5)	2(6)	-2(5)
C(20)	79(10)	72(8)	66(10)	-30(7)	-6(7)	-12(7)
C(21)	93(12)	101(11)	96(13)	-27(10)	-21(10)	-3(10)
C(22)	86(12)	87(11)	130(17)	-7(11)	-16(12)	11(9)

C(23)	91(12)	96(11)	85(13)	-15(9)	12(9)	7(9)
C(24)	105(12)	67(8)	46(9)	-5(6)	6(8)	-8(8)
C(25)	84(9)	56(7)	32(7)	-7(5)	1(6)	-12(6)
C(26)	103(12)	155(16)	102(14)	-88(13)	-35(10)	48(12)
C(27)	95(13)	182(19)	142(18)	-103(16)	-65(12)	46(13)
C(28)	76(11)	104(12)	137(17)	-20(11)	-15(11)	28(10)
C(29)	109(13)	60(9)	109(14)	-12(9)	-5(10)	6(9)
C(30)	101(11)	43(7)	90(11)	-15(7)	-24(8)	3(7)
C(31)	66(8)	56(7)	38(7)	-2(6)	-15(6)	17(6)
C(32)	103(11)	60(8)	68(11)	-4(7)	-22(9)	-10(8)
C(33)	98(12)	95(11)	84(13)	14(10)	-9(10)	-15(10)
C(34)	58(9)	130(14)	91(13)	12(11)	7(8)	23(10)
C(35)	109(14)	116(14)	101(15)	-26(11)	31(11)	-7(11)
C(36)	108(12)	71(9)	80(11)	-36(8)	-4(9)	-4(8)
C(37)	63(8)	54(7)	33(7)	-10(5)	2(5)	-14(6)
C(38)	77(11)	83(10)	123(15)	-30(10)	-2(9)	-2(9)
C(39)	69(11)	122(15)	159(20)	-33(14)	-27(11)	15(11)
C(40)	105(15)	136(17)	91(14)	-31(12)	-2(10)	62(13)
C(41)	123(14)	68(9)	68(11)	10(7)	8(9)	30(9)
C(42)	70(9)	68(8)	65(10)	7(7)	9(7)	7(7)
C(43)	90(9)	39(6)	51(8)	-13(6)	-25(7)	1(6)
C(44)	78(10)	89(10)	59(10)	0(7)	-9(8)	5(8)
C(45)	132(17)	127(15)	85(13)	-22(11)	27(13)	4(13)
C(46)	91(15)	103(14)	185(25)	-51(15)	18(15)	6(11)
C(47)	74(13)	104(14)	239(31)	-57(18)	-29(16)	2(11)
C(48)	104(13)	81(10)	107(14)	0(9)	-52(11)	2(9)
C(49)	85(9)	42(6)	31(7)	-11(5)	-13(6)	1(6)
C(50)	81(9)	51(7)	71(10)	-19(7)	-7(7)	3(7)
C(51)	98(11)	52(7)	72(10)	-17(7)	-21(8)	11(7)
C(52)	103(11)	84(10)	58(10)	-27(8)	-13(8)	36(9)
C(53)	128(14)	89(11)	71(11)	2(9)	32(10)	14(10)
C(54)	105(11)	62(8)	57(9)	-9(7)	35(8)	-24(8)
C(55)	105(10)	46(6)	33(7)	-7(5)	-3(7)	7(7)
C(56)	88(11)	97(11)	74(12)	-30(9)	-10(9)	-4(9)
C(57)	119(15)	95(11)	83(13)	-22(10)	24(11)	-6(10)
C(58)	74(10)	80(10)	140(18)	-7(11)	16(12)	5(8)
C(59)	103(13)	115(13)	88(13)	-23(10)	-33(11)	4(11)
C(60)	83(11)	99(10)	57(10)	-16(8)	-12(7)	2(8)
C(61)	67(8)	52(7)	41(7)	-14(6)	1(6)	-7(6)
C(62)	99(11)	88(10)	81(11)	-48(9)	-35(9)	19(9)
C(63)	104(13)	130(15)	149(18)	-73(14)	-38(12)	15(12)
C(64)	79(10)	110(12)	83(12)	-1(9)	-17(9)	-4(9)
C(65)	98(11)	55(8)	128(15)	-30(9)	-19(10)	13(8)
C(66)	110(11)	49(7)	76(11)	-23(7)	-15(8)	-2(8)
C(67)	71(8)	56(7)	39(7)	-6(6)	-14(6)	5(6)
C(68)	91(10)	55(8)	83(11)	1(7)	-2(8)	-12(7)

C(69)	87(11)	83(10)	88(13)	11(9)	-6(9)	-26(9)
C(70)	80(11)	136(15)	88(13)	-21(11)	7(9)	6(11)
C(71)	99(14)	106(14)	172(21)	-61(14)	8(13)	-12(11)
C(72)	78(10)	95(11)	98(12)	-46(10)	11(9)	-4(8)

Table 53. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for (P6).

Atom	x	y	z	U(eq)
H(2)	3026(12)	2577(6)	4090(5)	102
H(3)	4323(8)	1349(11)	4514(6)	135
H(4)	3403(14)	-165(8)	4801(5)	119
H(5)	1186(14)	-451(5)	4665(5)	90
H(6)	-111(8)	777(9)	4241(5)	84
H(8)	-896(12)	2494(9)	4891(5)	90
H(9)	-3032(17)	2634(10)	5345(3)	104
H(10)	-4910(10)	3014(11)	4884(7)	138
H(11)	-4652(11)	3255(10)	3969(7)	124
H(12)	-2516(15)	3115(9)	3515(3)	98
H(14)	-927(13)	4692(5)	4380(5)	94
H(15)	-2181(12)	5737(10)	4892(4)	115
H(16)	-1828(12)	7399(9)	4731(5)	101
H(17)	-221(15)	8015(4)	4059(5)	100
H(18)	1033(12)	6970(7)	3548(4)	88
H(20)	2846(13)	5394(9)	4323(3)	84
H(21)	5091(15)	5721(10)	4396(5)	113
H(22)	6708(8)	5668(10)	3677(7)	122
H(23)	6080(12)	5287(10)	2886(5)	110
H(24)	3836(15)	4960(9)	2813(3)	88
H(26)	-1650(15)	4740(9)	1723(6)	136
H(27)	-3521(14)	5682(13)	1480(6)	156
H(28)	-4063(12)	7115(11)	1840(6)	127
H(29)	-2733(15)	7606(7)	2442(6)	112
H(30)	-862(13)	6664(9)	2684(5)	92
H(32)	2316(15)	6555(7)	1993(5)	91
H(33)	3875(14)	7005(8)	1271(6)	113
H(34)	4386(12)	5966(12)	635(5)	117
H(35)	3340(16)	4477(11)	722(5)	133
H(36)	1782(14)	4027(6)	1445(6)	101
H(38)	-2679(13)	2266(8)	1198(6)	112
H(39)	-4258(7)	3437(13)	907(7)	137
H(40)	-3539(14)	4932(11)	474(6)	134
H(41)	-1242(17)	5256(6)	333(5)	108
H(42)	337(8)	4085(8)	624(5)	85
H(44)	983(13)	2539(10)	60(5)	91
H(45)	2982(21)	2555(12)	-500(3)	140
H(46)	5033(13)	2155(12)	-158(9)	151
H(47)	5085(11)	1739(11)	744(10)	162
H(48)	3086(19)	1724(10)	1304(4)	114

H(50)	-700(11)	-2104(7)	1415(4)	80
H(51)	451(13)	-3166(4)	886(5)	87
H(52)	2014(13)	-2575(8)	191(4)	97
H(53)	2426(12)	-922(9)	26(4)	121
H(54)	1276(13)	140(5)	556(5)	93
H(56)	-3200(16)	-118(10)	2224(3)	101
H(57)	-5499(14)	-366(11)	2220(5)	121
H(58)	-6347(8)	-635(10)	1446(7)	121
H(59)	-4895(15)	-656(11)	677(5)	120
H(60)	-2596(13)	-408(10)	681(3)	95
H(62)	1640(14)	-229(9)	3464(5)	102
H(63)	3476(15)	-1190(12)	3726(5)	146
H(64)	4336(11)	-2414(10)	3240(6)	109
H(65)	3360(14)	-2676(8)	2491(5)	110
H(66)	1524(14)	-1715(9)	2229(4)	92
H(68)	-1790(14)	-1730(6)	3061(5)	93
H(69)	-3554(14)	-2040(7)	3724(6)	105
H(70)	-4400(12)	-813(12)	4211(5)	122
H(71)	-3480(15)	723(10)	4034(6)	148
H(72)	-1715(14)	1032(6)	3371(6)	106
H(73A)	3375(20)	1003(13)	2459(13)	286
H(73B)	2962(20)	1183(13)	3046(13)	286
H(74A)	4894(24)	1898(19)	3103(12)	252
H(74B)	5441(24)	1291(19)	2647(12)	252
H(75A)	5547(22)	2641(21)	2029(12)	286
H(75B)	5623(22)	3202(21)	2528(12)	286
H(76A)	3423(19)	3520(17)	2609(18)	394
H(76B)	3479(19)	3343(17)	2023(18)	394

APPENDIX 2: NOTES ON $(Ph_3SiOH)_2 \cdot 18\text{-CROWN-}6 \cdot (H_2O)_2$ (C4)

A crystal of approximate dimensions 0.25 x 0.3 x 0.2 mm was used for data collection.

Crystal data: $C_{24}\ H_{30}\ O_5\ Si$, M = 426.57, Triclinic , a = 9.237(2), b = 10.902(2), c = 12.732(3) Å , α = 97.35(2), β = 107.35(2), γ = 95.49(3)°, U = 1201.6(4) Å^3, space group P-1(No.2), Z = 2, D_c = 1.179 g cm^{-3}, (mMo-K_a) = 0.128 mm^{-1}, F(000) = 456. Crystallographic measurements were made at 293(2)° K on a CAD4 automatic four-circle diffractometer in the range 2.33<q<23.92°. Data (4034 reflections) were corrected for Lorentz and polarization but not for absorption.

In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant except for the alcoholic proton (H4, bonded to O4) and the water protons (H5 & H6, bonded to O5), which were located and refined at fixed distances of 0.96(3) Å from the relevant parent atoms. In addition, H5 and H6 were constrained to maintain a distance of 1.40(3) Å from each other.

The asymmetric unit (unprimed labelled atoms in figure 68) consists of 1 triphenylsilanol molecule, 1 water molecule and ½ of one crown ether. The remaining portion of the crown is afforded by the symmetry operation 2-x, 1-y, 2-z.

Examination of the supramolecular structure for this molecule exhibited some interesting features. Typically, H4 hydrogen-bonds to the water molecule in the asymmetric unit as presented, whereas the water protons (H5 and H6) interact with O2 and O3 of the crown fragments generated as a consequence of the symmetry operators -1+x, y, -1+z and 1-x, 1-y, 1-z respectively. The combination of these intra- and intermolecular contacts serves to afford discrete hydrogen-bonded units within the lattice array, as exhibited in figure 54, where it can be clearly seen that each crown ether moiety and its associated water molecules are sandwiched between 2 offset triphenyl silanols. However, figure 55 illustrates that when looking along the a vector, the crowns are aligned, albeit at an oblique angle.

The solution of the structure (SHELX86)[1] and refinement (SHELX93)[2] converged to a conventional [i.e. based on 2356 with Fo>4s(Fo)] $R1$ = 0.0430 and $wR2$ = 0.1039. Goodness of fit = 1.145. The max. and min. residual densities were 0.166 and -0.163eÅ^{-3} respectively. The asymmetric unit (shown in figure 54), along with the labelling scheme used was produced using ORTEX.[3] Final fractional atomic co-ordinates and isotropic thermal parameters, bond distances and angles are given in Tables 55, 56 and 57 respectively. Tables of anisotropic temperature factors are available as supplementary data.

1. Sheldrick G.M., Acta Cryst., A46, 467-73, 1990.
2. Sheldrick G.M., J.Appl.Cryst., 1995 (In preparation.)
3. McArdle P., J.Appl.Cryst., 27, 438, 1994

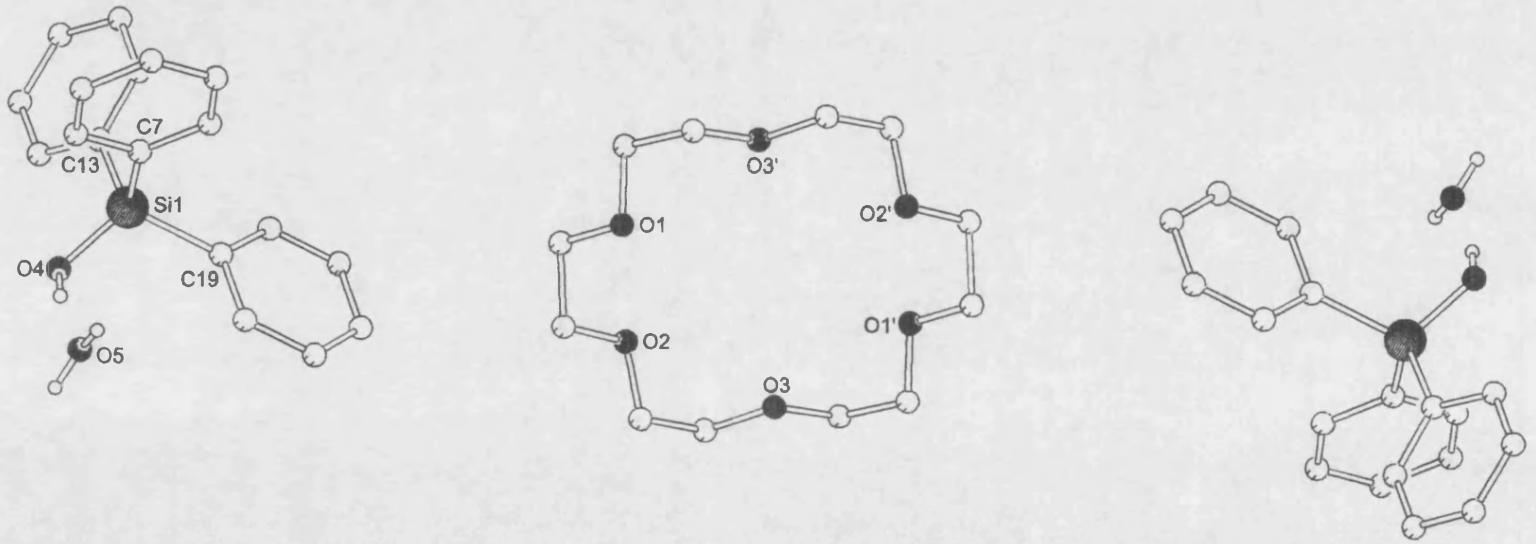

Figure 68 The asymmetric unit of $(Ph_3SiOH)_2 \cdot 18\text{-crown-}6 \cdot (H_2O)_2$ **(C4)**

Table 54. Crystal data and structure refinement for (C4).

Empirical formula	$C_{24}\ H_{30}O_5\ Si$
Formula weight	426.57
Temperature	293(2)° K
Wavelength	0.70930 Å
Crystal system	Triclinic
Space group	P-1(No.2)
Unit cell dimensions	a = 9.237(2)Å α= 97.35(2)°
	b = 10.902(2)Å β= 107.35(2)°
	c = 12.732(3)Å γ= 95.49(3)°
Volume	1201.6(4) $Å^3$
Z	2
Density (calculated)	1.179 Mg/m^3
Absorption coefficient	0.128 mm^{-1}
F(000)	456
Crystal size	0.25 x 0.3 x 0.2 mm
Theta range for data collection	2.33 to 23.92°
Index ranges	0<=h<=10; -12<=k<=12; -14<=l<=13
Reflections collected	4034
Independent reflections	3770 [R(int) = 0.0180]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3763 / 4 / 284
Goodness-of-fit on F^2	1.145
Final R indices [I>2σ(I)]	R1 = 0.0430 wR2 = 0.1039
R indices (all data)	R1 = 0.0995 wR2 = 0.1298
Largest diff. peak and hole	0.166 and -0.163 $eÅ^{-3}$
Weighting scheme	calc $w=1/[\sigma^2(Fo^2)+(0.0543P)^2+0.3241P]$ where $P=(Fo^2+2Fc^2)/3$
Extinction coefficient	0.0188(25)

Table 55. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for (C4). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Si(1)	3887(1)	8966(1)	2151(1)	43(1)
O(1)	8043(3)	6236(2)	8401(2)	72(1)
O(2)	10511(3)	5194(2)	7892(2)	70(1)
O(3)	11841(3)	3498(2)	9332(2)	75(1)
O(4)	3501(3)	8453(2)	833(2)	61(1)
O(5)	1231(3)	6473(3)	211(2)	81(1)
C(1)	8682(5)	6608(4)	7610(3)	91(1)
C(2)	9218(4)	5515(4)	7100(3)	88(1)
C(3)	10911(5)	4047(4)	7544(3)	86(1)
C(4)	12259(5)	3776(4)	8391(4)	89(1)
C(5)	13067(4)	3224(4)	10186(4)	94(1)
C(6)	12481(5)	2775(4)	11048(4)	91(1)
C(7)	2086(3)	9186(2)	2487(2)	44(1)
C(8)	874(3)	9570(3)	1713(3)	64(1)
C(9)	-433(4)	9821(3)	1955(4)	83(1)
C(10)	-576(4)	9680(4)	2967(4)	86(1)
C(11)	575(4)	9280(3)	3745(3)	77(1)
C(12)	1898(3)	9031(3)	3500(3)	59(1)
C(13)	5103(3)	10515(2)	2470(2)	41(1)
C(14)	5815(3)	10952(3)	1733(2)	50(1)
C(15)	6703(4)	12117(3)	2006(3)	64(1)
C(16)	6902(4)	12859(3)	2995(3)	68(1)
C(17)	6214(4)	12457(3)	3734(3)	66(1)
C(18)	5325(3)	11308(3)	3466(2)	53(1)
C(19)	4911(3)	7872(2)	3037(2)	43(1)
C(20)	4382(3)	6595(3)	2775(3)	57(1)
C(21)	5090(4)	5768(3)	3420(3)	67(1)
C(22)	6350(4)	6185(3)	4327(3)	66(1)
C(23)	6911(4)	7440(3)	4608(3)	63(1)
C(24)	6197(3)	8268(3)	3957(2)	51(1)

Table 56. Bond lengths [Å] and angles [°] for **(C4)**.

Si(1)-O(4)	1.620(2)
Si(1)-C(13)	1.862(3)
Si(1)-C(7)	1.866(3)
Si(1)-C(19)	1.874(3)
O(1)-C(1)	1.393(4)
O(1)-C(6)#1	1.413(4)
O(2)-C(3)	1.393(4)
O(2)-C(2)	1.420(4)
O(3)-C(5)	1.402(4)
O(3)-C(4)	1.422(4)
C(1)-C(2)	1.480(6)
C(3)-C(4)	1.467(5)
C(5)-C(6)	1.477(5)
C(6)-O(1)#1	1.413(4)
C(7)-C(12)	1.380(4)
C(7)-C(8)	1.392(4)
C(8)-C(9)	1.375(5)
C(9)-C(10)	1.360(5)
C(10)-C(11)	1.369(5)
C(11)-C(12)	1.390(4)
C(13)-C(18)	1.388(4)
C(13)-C(14)	1.401(4)
C(14)-C(15)	1.387(4)
C(15)-C(16)	1.359(5)
C(16)-C(17)	1.375(5)
C(17)-C(18)	1.374(4)
C(19)-C(24)	1.383(4)
C(19)-C(20)	1.394(4)
C(20)-C(21)	1.378(4)
C(21)-C(22)	1.363(4)
C(22)-C(23)	1.377(4)
C(23)-C(24)	1.384(4)
H(4)-O(5)	1.82(3)
H(5)-O(2)#2	2.08(3)
H(6)-O(3)#3	2.22(3)
O(4)-Si(1)-C(13)	107.60(12)
O(4)-Si(1)-C(7)	110.23(12)
C(13)-Si(1)-C(7)	108.38(12)
O(4)-Si(1)-C(19)	111.95(12)
C(13)-Si(1)-C(19)	109.96(12)
C(7)-Si(1)-C(19)	108.67(12)
C(1)-O(1)-C(6)#1	112.8(3)
C(3)-O(2)-C(2)	113.1(3)
C(5)-O(3)-C(4)	113.2(3)

O(1)-C(1)-C(2)	108.5(3)
O(2)-C(2)-C(1)	109.8(3)
O(2)-C(3)-C(4)	110.4(3)
O(3)-C(4)-C(3)	109.4(3)
O(3)-C(5)-C(6)	109.1(3)
O(1)#1-C(6)-C(5)	109.6(3)
C(12)-C(7)-C(8)	116.9(3)
C(12)-C(7)-Si(1)	123.2(2)
C(8)-C(7)-Si(1)	119.9(2)
C(9)-C(8)-C(7)	121.7(3)
C(10)-C(9)-C(8)	120.1(3)
C(9)-C(10)-C(11)	120.1(3)
C(10)-C(11)-C(12)	119.7(4)
C(7)-C(12)-C(11)	121.5(3)
C(18)-C(13)-C(14)	116.6(3)
C(18)-C(13)-Si(1)	120.5(2)
C(14)-C(13)-Si(1)	122.9(2)
C(15)-C(14)-C(13)	120.8(3)
C(16)-C(15)-C(14)	120.7(3)
C(15)-C(16)-C(17)	119.9(3)
C(18)-C(17)-C(16)	119.7(3)
C(17)-C(18)-C(13)	122.3(3)
C(24)-C(19)-C(20)	117.1(3)
C(24)-C(19)-Si(1)	123.1(2)
C(20)-C(19)-Si(1)	119.9(2)
C(21)-C(20)-C(19)	121.4(3)
C(22)-C(21)-C(20)	120.3(3)
C(21)-C(22)-C(23)	119.9(3)
C(22)-C(23)-C(24)	119.6(3)
C(19)-C(24)-C(23)	121.7(3)
O(4)-H(4)-O(5)	170(3)
O(5)-H(5)-O(2)#2	170(4)
O(5)-H(6)-O(3)#3	160(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2, -y+1, -z+2

#2 -1+x, y, -1+z

#3 1-x, 1-y, 1-z

Table 57. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **(C4)**.

The anisotropic displacement factor exponent takes the form:

$-2\,pi^2\,[\,h^2\,a^*\,2\,U11 + ... + 2\,h\,k\,a^*\,b^*\,U12\,]$

Atom	U11	U22	U33	U23	U13	U12
Si(1)	42(1)	42(1)	44(1)	6(1)	16(1)	5(1)
O(1)	65(1)	74(2)	75(2)	23(1)	16(1)	9(1)
O(2)	71(2)	68(2)	65(2)	4(1)	20(1)	-1(1)
O(3)	64(2)	80(2)	90(2)	14(1)	32(1)	21(1)
O(4)	65(1)	66(2)	47(1)	1(1)	20(1)	-2(1)
O(5)	66(2)	80(2)	78(2)	-10(2)	12(1)	-11(1)
C(1)	80(3)	109(3)	82(3)	44(3)	14(2)	14(2)
C(2)	68(2)	133(4)	57(2)	26(2)	10(2)	-1(2)
C(3)	101(3)	89(3)	73(3)	3(2)	44(2)	0(2)
C(4)	99(3)	82(3)	114(3)	14(2)	73(3)	23(2)
C(5)	68(2)	108(3)	110(3)	17(3)	28(2)	40(2)
C(6)	86(3)	82(3)	107(3)	30(2)	17(2)	41(2)
C(7)	39(2)	38(2)	53(2)	2(1)	15(1)	1(1)
C(8)	51(2)	70(2)	75(2)	20(2)	21(2)	14(2)
C(9)	53(2)	87(3)	117(3)	26(2)	28(2)	28(2)
C(10)	54(2)	82(3)	131(4)	1(2)	49(3)	15(2)
C(11)	78(3)	79(3)	83(3)	-3(2)	47(2)	9(2)
C(12)	53(2)	64(2)	61(2)	1(2)	24(2)	8(2)
C(13)	39(2)	42(2)	47(2)	12(1)	16(1)	11(1)
C(14)	45(2)	57(2)	53(2)	14(1)	20(1)	13(1)
C(15)	60(2)	62(2)	84(2)	30(2)	35(2)	8(2)
C(16)	66(2)	45(2)	92(3)	14(2)	24(2)	-4(2)
C(17)	82(2)	46(2)	66(2)	1(2)	23(2)	3(2)
C(18)	64(2)	45(2)	53(2)	10(1)	26(2)	3(2)
C(19)	42(2)	41(2)	52(2)	6(1)	22(1)	8(1)
C(20)	48(2)	47(2)	70(2)	7(2)	12(2)	5(1)
C(21)	66(2)	45(2)	84(2)	14(2)	13(2)	9(2)
C(22)	69(2)	59(2)	78(2)	26(2)	24(2)	23(2)
C(23)	62(2)	64(2)	57(2)	14(2)	9(2)	11(2)
C(24)	55(2)	45(2)	55(2)	6(1)	20(2)	4(1)

Table 58. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (C4).

Atom	x	y	z	U(eq)
H(4)	2732(32)	7807(26)	539(26)	75(11)
H(5)	992(51)	6006(40)	-445(26)	140(20)
H(6)	459(43)	6382(44)	476(34)	139(21)
H(1A)	9536(5)	7270(4)	7962(3)	109
H(1B)	7924(5)	6922(4)	7040(3)	109
H(2A)	8402(4)	4812(4)	6852(3)	106
H(2B)	9492(4)	5711(4)	6456(3)	106
H(3A)	11132(5)	4065(4)	6848(3)	103
H(3B)	10059(5)	3392(4)	7416(3)	103
H(4A)	12655(5)	3070(4)	8084(4)	107
H(4B)	13056(5)	4492(4)	8615(4)	107
H(5A)	13813(4)	3968(4)	10512(4)	112
H(5B)	13566(4)	2588(4)	9883(4)	112
H(6A)	11647(5)	2095(4)	10705(4)	110
H(6B)	13289(5)	2463(4)	11583(4)	110
H(8)	950(3)	9660(3)	1014(3)	77
H(9)	-1221(4)	10087(3)	1426(4)	100
H(10)	-1458(4)	9856(4)	3131(4)	103
H(11)	474(4)	9176(3)	4435(3)	92
H(12)	2673(3)	8754(3)	4030(3)	70
H(14)	5690(3)	10455(3)	1053(2)	60
H(15)	7167(4)	12393(3)	1507(3)	77
H(16)	7503(4)	13637(3)	3172(3)	82
H(17)	6350(4)	12961(3)	4413(3)	79
H(18)	4854(3)	11053(3)	3968(2)	64
H(20)	3533(3)	6295(3)	2151(3)	69
H(21)	4706(4)	4921(3)	3236(3)	81
H(22)	6831(4)	5622(3)	4757(3)	79
H(23)	7764(4)	7729(3)	5230(3)	75
H(24)	6593(3)	9112(3)	4143(2)	61

APPENDIX 3: NOTES ON $(Ph_3SiOH)_2$·MONOAZACROWN·(H_2O)

A crystal of approximate dimensions 0.35 x 0.35 x 0.3 mm was used for data collection.

Crystal data: C_{48} H_{59} N O_8 Si_2, M = 834.14, Triclinic , a = 12.601(3), b = 13.989(2), c = 15.024(2) Å , α = 78.62(2), β = 87.97(2), γ = 64.83(2)°, U = 2346.3(7) Å^3, space group P-1(No.2), Z = 2, D_c = 1.181 g cm^{-3}, (mMo-K_a) = 0.127 mm^{-1}, F(000) = 892. Crystallographic measurements were made at 293(2)° K on a CAD4 automatic four-circle diffractometer in the range 2.15<q<23.92°. Data (7720 reflections) were corrected for Lorentz and polarization but not for absorption.

In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant, except in the case of H1A, H1B, and H2A, (attached to O1, O2, N1 respectively) and also H8A and H8B (attached to the water oxygen, O8). These protons were located in an advanced Difference Fourier map and refined at a distance of 0.88 Å from the relevant parent atoms.

The ease of locating these outstanding hydrogen atoms may be partially attributed to the fact that they are engaged in intermolecular hydrogen bonding. Typically, H2A bonds to N1 of the asymmetric unit as presented, while H8A and H8B have an affinity for crown oxygens O6 and O4 respectively. [H2A - N1, 1.95(2), H8B - O4, 2.11(2), H8A - O6, 2.22(2) Å; O2 - H2A - N1, 167 (3), O8 - H8B - O4, 167 (3), O8 - H8A - O6, 173 (3)°] In addition, H1A interacts with O8 of the molecule generated via the *x, -1+y, z* operator. [H1A - O8, 1.95(2) Å, O1 - H1A - O8, 180(3)°]. The net consequence of these contacts is, that each crown (and its associated water molecule) is sandwiched between 2 triphenylsilanols to yield discrete hydrogen-bonded entities which dominate the supramolecular structure.

The solution of the structure (SHELX86)[1] and refinement (SHELX93)[2] converged to a conventional [i.e. based on 4124 with $Fo>4s(Fo)$] $R1$ = 0.0469 and $wR2$ = 0.0859. Goodness of fit = 1.102. The max. and min. residual densities were 0.191 and -0.182eÅ^{-3} respectively. The asymmetric unit (shown in Figure 56), along with the labelling scheme used was produced using ORTEX.[3] Final fractional atomic co-ordinates and isotropic thermal parameters, bond distances and angles are given in Tables 60 , 61 and 62 respectively. Tables of anisotropic temperature factors are available as supplementary data.

1. Sheldrick G.M., Acta Cryst., A46, 467-73, 1990.
2. Sheldrick G.M., J.Appl.Cryst., 1995 (In preparation.)
3. McArdle P., J.Appl.Cryst., 27, 438, 1994

Table 59. Crystal data and structure refinement for (C6).

Empirical formula	$C_{48}H_{59}NO_8Si_2$
Formula weight	834.14
Temperature	293(2)° K
Wavelength	0.70930 Å
Crystal system	Triclinic
Space group	P-1(No.2)
Unit cell dimensions	a = 12.601(3)Å alpha = 78.62(2)°
	b = 13.989(2)Å beta = 87.97(2)°
	c = 15.024(2)Å gamma = 64.83(2)°
Volume	2346.3(7) $Å^3$
Z	2
Density (calculated)	1.181 Mg m^{-3}
Absorption coefficient	0.127 mm^{-1}
F(000)	892
Crystal size	0.35 x 0.35 x 0.3 mm
Theta range for data collection	2.15 to 23.92°
Index ranges	-14<=h<=0; -15<=k<=14; -17<=l<=17
Reflections collected	7720
Independent reflections	7337 [R(int) = 0.0192]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7323 / 5 / 548
Goodness-of-fit on F^2	1.102
Final R indices [I>2σ(I)]	R1 = 0.0469 wR2 = 0.0859
R indices (all data)	R1 = 0.1211 wR2 = 0.1150
Largest diff. peak and hole	0.191 and -0.182 e.A-3
Weighting scheme	calc $w=1/[\sigma^2(Fo^2)+(0.0321P)^2+0.9771P]$ where $P=(Fo^2+2Fc^2)/3$
Extinction coefficient	0.0053(4)

Table 60. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for (C6). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Si(1)	1137(1)	6247(1)	7421(1)	47(1)
Si(2)	4268(1)	8981(1)	7427(1)	45(1)
O(1)	335(2)	5611(2)	7346(2)	62(1)
O(2)	5053(2)	9627(2)	7485(2)	59(1)
N(1)	4515(2)	11754(2)	7532(2)	60(1)
O(3)	3216(2)	12838(2)	5821(2)	68(1)
O(4)	936(2)	12936(2)	5954(2)	77(1)
O(5)	-350(2)	13079(2)	7542(2)	78(1)
O(6)	1061(2)	12385(2)	9200(2)	77(1)
O(7)	3347(2)	12159(2)	9198(2)	80(1)
O(8)	1819(2)	13454(2)	7491(2)	65(1)
C(1)	112(2)	7607(2)	7614(2)	45(1)
C(2)	-1094(2)	8019(2)	7458(2)	53(1)
C(3)	-1847(3)	9003(3)	7641(2)	62(1)
C(4)	-1415(3)	9614(3)	7972(2)	70(1)
C(5)	-229(3)	9243(3)	8134(3)	80(1)
C(6)	515(3)	8244(3)	7964(2)	68(1)
C(7)	1953(2)	6336(2)	6373(2)	47(1)
C(8)	1973(3)	7283(3)	5896(2)	59(1)
C(9)	2617(3)	7303(3)	5133(2)	71(1)
C(10)	3264(3)	6366(3)	4835(2)	71(1)
C(11)	3252(3)	5420(3)	5285(2)	68(1)
C(12)	2612(3)	5405(2)	6043(2)	58(1)
C(13)	2209(3)	5547(2)	8419(2)	51(1)
C(14)	1797(3)	5344(3)	9269(2)	74(1)
C(15)	2536(5)	4820(3)	10030(3)	100(1)
C(16)	3702(5)	4485(3)	9975(3)	106(2)
C(17)	4146(4)	4675(3)	9151(4)	103(2)
C(18)	3406(3)	5202(3)	8372(3)	75(1)
C(19)	5312(2)	7594(2)	7292(2)	45(1)
C(20)	4928(3)	6940(2)	6947(2)	62(1)
C(21)	5675(3)	5913(3)	6864(2)	73(1)
C(22)	6839(3)	5511(3)	7117(2)	72(1)
C(23)	7257(3)	6132(3)	7455(2)	66(1)
C(24)	6494(3)	7166(2)	7547(2)	53(1)
C(25)	3200(2)	9585(2)	6419(2)	45(1)
C(26)	2008(3)	9887(2)	6472(2)	58(1)
C(27)	1254(3)	10280(3)	5702(3)	71(1)
C(28)	1690(4)	10377(3)	4857(3)	74(1)

C(29)	2867(4)	10083(3)	4781(2)	73(1)
C(30)	3607(3)	9690(2)	5546(2)	60(1)
C(31)	3440(2)	8878(2)	8474(2)	44(1)
C(32)	2737(3)	9782(2)	8827(2)	58(1)
C(33)	2108(3)	9711(3)	9584(2)	69(1)
C(34)	2171(3)	8735(3)	10016(2)	70(1)
C(35)	2849(3)	7824(3)	9695(2)	67(1)
C(36)	3472(3)	7900(2)	8929(2)	55(1)
C(37)	4979(3)	12160(3)	6719(3)	77(1)
C(38)	4425(3)	12128(3)	5874(3)	77(1)
C(39)	2594(4)	12775(3)	5098(2)	85(1)
C(40)	1316(4)	13415(3)	5166(3)	90(1)
C(41)	-286(3)	13298(3)	5960(3)	91(1)
C(42)	-579(3)	12724(3)	6789(3)	88(1)
C(43)	-605(4)	12592(3)	8369(3)	96(1)
C(44)	-177(4)	12907(3)	9121(3)	93(1)
C(45)	1541(4)	12631(3)	9897(3)	90(1)
C(46)	2820(4)	11954(3)	10013(2)	93(1)
C(47)	4549(4)	11464(3)	9205(3)	89(1)
C(48)	5038(3)	11832(3)	8360(3)	82(1)

Table 61. Bond lengths [Å] and angles [°] for (C6).

Si(1)-O(1)	1.625(2)	C(25)-Si(2)-C(19)	107.19(13)
Si(1)-C(7)	1.862(3)	O(2)-Si(2)-C(31)	112.57(12)
Si(1)-C(1)	1.863(3)	C(25)-Si(2)-C(31)	108.44(13)
Si(1)-C(13)	1.863(3)	C(19)-Si(2)-C(31)	109.14(13)
Si(2)-O(2)	1.613(2)	C(37)-N(1)-C(48)	111.2(3)
Si(2)-C(25)	1.868(3)	C(39)-O(3)-C(38)	112.8(3)
Si(2)-C(19)	1.871(3)	C(41)-O(4)-C(40)	113.7(3)
Si(2)-C(31)	1.872(3)	C(43)-O(5)-C(42)	113.9(3)
N(1)-C(37)	1.455(4)	C(45)-O(6)-C(44)	113.2(3)
N(1)-C(48)	1.471(4)	C(47)-O(7)-C(46)	113.6(3)
O(3)-C(39)	1.400(4)	C(6)-C(1)-C(2)	116.2(3)
O(3)-C(38)	1.416(4)	C(6)-C(1)-Si(1)	121.3(2)
O(4)-C(41)	1.401(4)	C(2)-C(1)-Si(1)	122.4(2)
O(4)-C(40)	1.414(4)	C(3)-C(2)-C(1)	121.9(3)
O(5)-C(43)	1.392(4)	C(4)-C(3)-C(2)	120.1(3)
O(5)-C(42)	1.405(4)	C(3)-C(4)-C(5)	120.0(3)
O(6)-C(45)	1.395(4)	C(4)-C(5)-C(6)	119.2(3)
O(6)-C(44)	1.412(4)	C(5)-C(6)-C(1)	122.4(3)
O(7)-C(47)	1.408(4)	C(8)-C(7)-C(12)	116.5(3)
O(7)-C(46)	1.409(4)	C(8)-C(7)-Si(1)	124.0(2)
C(1)-C(6)	1.385(4)	C(12)-C(7)-Si(1)	119.5(2)
C(1)-C(2)	1.387(4)	C(9)-C(8)-C(7)	121.8(3)
C(2)-C(3)	1.376(4)	C(10)-C(9)-C(8)	119.8(3)
C(3)-C(4)	1.363(4)	C(11)-C(10)-C(9)	119.8(3)
C(4)-C(5)	1.370(4)	C(10)-C(11)-C(12)	120.1(3)
C(5)-C(6)	1.381(4)	C(11)-C(12)-C(7)	122.0(3)
C(7)-C(8)	1.387(4)	C(18)-C(13)-C(14)	116.8(3)
C(7)-C(12)	1.392(4)	C(18)-C(13)-Si(1)	124.3(3)
C(8)-C(9)	1.385(4)	C(14)-C(13)-Si(1)	118.9(2)
C(9)-C(10)	1.370(4)	C(15)-C(14)-C(13)	122.1(4)
C(10)-C(11)	1.368(4)	C(16)-C(15)-C(14)	120.5(4)
C(11)-C(12)	1.373(4)	C(15)-C(16)-C(17)	119.4(4)
C(13)-C(18)	1.378(4)	C(16)-C(17)-C(18)	120.6(4)
C(13)-C(14)	1.385(4)	C(13)-C(18)-C(17)	120.6(4)
C(14)-C(15)	1.369(5)	C(24)-C(19)-C(20)	117.0(3)
C(15)-C(16)	1.344(6)	C(24)-C(19)-Si(2)	121.8(2)
C(16)-C(17)	1.365(6)	C(20)-C(19)-Si(2)	121.3(2)
C(17)-C(18)	1.390(5)	C(21)-C(20)-C(19)	122.1(3)
C(19)-C(24)	1.384(4)	C(22)-C(21)-C(20)	119.8(3)
C(19)-C(20)	1.385(4)	C(21)-C(22)-C(23)	120.1(3)
C(20)-C(21)	1.370(4)	C(22)-C(23)-C(24)	119.7(3)
C(21)-C(22)	1.366(5)	C(19)-C(24)-C(23)	121.3(3)
C(22)-C(23)	1.369(5)	C(26)-C(25)-C(30)	116.2(3)
C(23)-C(24)	1.386(4)	C(26)-C(25)-Si(2)	123.9(2)
C(25)-C(26)	1.381(4)	C(30)-C(25)-Si(2)	119.8(2)

C(25)-C(30)	1.395(4)	C(25)-C(26)-C(27)	122.0(3)
C(26)-C(27)	1.388(4)	C(28)-C(27)-C(26)	119.9(3)
C(27)-C(28)	1.370(5)	C(29)-C(28)-C(27)	119.6(3)
C(28)-C(29)	1.368(5)	C(28)-C(29)-C(30)	120.2(3)
C(29)-C(30)	1.372(4)	C(29)-C(30)-C(25)	122.2(3)
C(31)-C(36)	1.389(4)	C(36)-C(31)-C(32)	116.4(3)
C(31)-C(32)	1.393(4)	C(36)-C(31)-Si(2)	121.7(2)
C(32)-C(33)	1.374(4)	C(32)-C(31)-Si(2)	121.9(2)
C(33)-C(34)	1.362(4)	C(33)-C(32)-C(31)	121.9(3)
C(34)-C(35)	1.368(4)	C(34)-C(33)-C(32)	120.0(3)
C(35)-C(36)	1.383(4)	C(33)-C(34)-C(35)	120.3(3)
C(37)-C(38)	1.487(5)	C(34)-C(35)-C(36)	119.6(3)
C(39)-C(40)	1.485(5)	C(35)-C(36)-C(31)	121.8(3)
C(41)-C(42)	1.469(5)	N(1)-C(37)-C(38)	112.0(3)
C(43)-C(44)	1.483(5)	O(3)-C(38)-C(37)	108.7(3)
C(45)-C(46)	1.476(5)	O(3)-C(39)-C(40)	109.6(3)
C(47)-C(48)	1.488(5)	O(4)-C(40)-C(39)	109.4(3)
H(1A) - O(8#1)	1.95(2)	O(4)-C(41)-C(42)	109.1(3)
H(2A) - N(1)	1.95(2)	O(5)-C(42)-C(41)	108.9(3)
H(8B) - O(4)	2.11(2)	O(5)-C(43)-C(44)	109.3(3)
H(8A) - O(6)	2.22(2)	O(6)-C(44)-C(43)	109.2(3)
		O(6)-C(45)-C(46)	109.9(3)
O(1)-Si(1)-C(7)	111.11(13)	O(7)-C(46)-C(45)	109.4(3)
O(1)-Si(1)-C(1)	106.23(12)	O(7)-C(47)-C(48)	108.7(3)
C(7)-Si(1)-C(1)	111.75(13)	N(1)-C(48)-C(47)	112.7(3)
O(1)-Si(1)-C(13)	110.37(13)	O1 - H(1A) - O(8#1)	180(3)
C(7)-Si(1)-C(13)	108.99(14)	O(2) - H(2A) - N(1)	167(3)
C(1)-Si(1)-C(13)	108.33(13)	O(8) - H(8B) - O(4)	167(3)
O(2)-Si(2)-C(25)	112.90(12)	O(8) - H(8A) - O(6)	173(3)
O(2)-Si(2)-C(19)	106.40(12)		

Symmetry transformations used to generate equivalent atoms:

#1 x, -1+y, z

Table 62. Anisotropic displacement parameters ($Å^2$ x 10^3) for (C6).

The anisotropic displacement factor exponent takes the form:

$-2\,pi^2\,[\,h^2\,a^*\,2\,U11 + ... + 2\,h\,k\,a^*\,b^*\,U12\,]$

Atom	U11	U22	U33	U23	U13	U12
Si(1)	40(1)	49(1)	50(1)	-12(1)	0(1)	-16(1)
Si(2)	41(1)	43(1)	49(1)	-10(1)	3(1)	-16(1)
O(1)	51(1)	58(1)	81(2)	-16(1)	0(1)	-24(1)
O(2)	49(1)	50(1)	82(2)	-18(1)	4(1)	-23(1)
N(1)	50(2)	53(2)	75(2)	-13(1)	6(2)	-20(1)
O(3)	81(2)	58(1)	58(2)	-15(1)	15(1)	-22(1)
O(4)	71(2)	82(2)	66(2)	-7(1)	-8(1)	-25(1)
O(5)	73(2)	78(2)	83(2)	-9(1)	11(1)	-35(1)
O(6)	90(2)	72(2)	59(2)	-18(1)	12(1)	-24(1)
O(7)	92(2)	82(2)	59(2)	-7(1)	-6(1)	-33(2)
O(8)	77(2)	70(2)	54(2)	-10(1)	6(1)	-38(1)
C(1)	42(2)	52(2)	40(2)	-10(1)	4(1)	-18(2)
C(2)	43(2)	62(2)	49(2)	-12(2)	-1(1)	-18(2)
C(3)	43(2)	67(2)	57(2)	-9(2)	0(2)	-8(2)
C(4)	64(2)	61(2)	73(2)	-26(2)	11(2)	-10(2)
C(5)	72(3)	73(3)	108(3)	-48(2)	11(2)	-30(2)
C(6)	44(2)	71(2)	90(3)	-34(2)	0(2)	-20(2)
C(7)	43(2)	49(2)	47(2)	-12(2)	-4(1)	-18(2)
C(8)	64(2)	54(2)	63(2)	-21(2)	8(2)	-28(2)
C(9)	84(3)	72(3)	68(2)	-8(2)	9(2)	-48(2)
C(10)	65(2)	91(3)	65(2)	-23(2)	22(2)	-40(2)
C(11)	69(2)	66(2)	64(2)	-25(2)	15(2)	-21(2)
C(12)	61(2)	52(2)	57(2)	-12(2)	9(2)	-20(2)
C(13)	52(2)	41(2)	55(2)	-11(2)	-5(2)	-14(2)
C(14)	72(2)	74(2)	56(2)	-6(2)	-4(2)	-15(2)
C(15)	123(4)	86(3)	63(3)	1(2)	-21(3)	-22(3)
C(16)	126(4)	76(3)	87(3)	-11(3)	-55(3)	-13(3)
C(17)	65(3)	101(3)	126(4)	-28(3)	-37(3)	-13(2)
C(18)	52(2)	84(3)	82(3)	-17(2)	-11(2)	-22(2)
C(19)	42(2)	46(2)	43(2)	-8(1)	5(1)	-16(1)
C(20)	51(2)	58(2)	76(2)	-26(2)	6(2)	-19(2)
C(21)	78(3)	63(2)	88(3)	-36(2)	22(2)	-31(2)
C(22)	75(3)	45(2)	74(3)	-10(2)	24(2)	-7(2)
C(23)	47(2)	66(2)	60(2)	-4(2)	4(2)	-5(2)
C(24)	49(2)	56(2)	48(2)	-9(2)	3(2)	-17(2)
C(25)	44(2)	38(2)	49(2)	-9(1)	2(1)	-13(1)
C(26)	53(2)	57(2)	56(2)	-9(2)	-1(2)	-15(2)
C(27)	53(2)	70(2)	78(3)	-15(2)	-12(2)	-13(2)
C(28)	86(3)	63(2)	61(2)	-8(2)	-25(2)	-21(2)

C(29)	91(3)	77(3)	44(2)	-8(2)	-1(2)	-30(2)
C(30)	61(2)	60(2)	55(2)	-11(2)	7(2)	-24(2)
C(31)	41(2)	46(2)	44(2)	-10(1)	-3(1)	-16(1)
C(32)	69(2)	49(2)	55(2)	-11(2)	11(2)	-25(2)
C(33)	85(3)	65(2)	61(2)	-26(2)	25(2)	-33(2)
C(34)	83(3)	78(3)	57(2)	-17(2)	23(2)	-41(2)
C(35)	79(2)	59(2)	63(2)	1(2)	7(2)	-33(2)
C(36)	54(2)	49(2)	58(2)	-10(2)	1(2)	-19(2)
C(37)	64(2)	67(2)	98(3)	-15(2)	22(2)	-28(2)
C(38)	82(3)	61(2)	79(3)	-15(2)	39(2)	-25(2)
C(39)	112(3)	86(3)	48(2)	-11(2)	11(2)	-35(3)
C(40)	111(4)	86(3)	61(3)	6(2)	-22(2)	-38(3)
C(41)	78(3)	101(3)	83(3)	-10(2)	-20(2)	-30(2)
C(42)	70(3)	93(3)	105(3)	-28(3)	-5(2)	-34(2)
C(43)	79(3)	103(3)	98(3)	4(3)	16(2)	-42(3)
C(44)	82(3)	93(3)	87(3)	-15(2)	37(2)	-26(2)
C(45)	127(4)	87(3)	57(2)	-21(2)	20(2)	-43(3)
C(46)	132(4)	101(3)	46(2)	-11(2)	-5(2)	-52(3)
C(47)	93(3)	90(3)	73(3)	-12(2)	-28(2)	-29(3)
C(48)	67(2)	84(3)	102(3)	-28(2)	-10(2)	-34(2)

Table 62. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (**C6**).

Atom	x	y	z	U(eq)
H(1A)	771(26)	4976(19)	7391(23)	75
H(2A)	4783(26)	10279(18)	7515(21)	71
H(1B)	3761(20)	12137(23)	7515(21)	72
H(8A)	1663(29)	13158(25)	7977(18)	78
H(8B)	1527(28)	13245(26)	7112(20)	78
H(2)	-1403(2)	7618(2)	7223(2)	63
H(3)	-2653(3)	9253(3)	7539(2)	74
H(4)	-1925(3)	10284(3)	8088(2)	84
H(5)	71(3)	9659(3)	8355(3)	96
H(6)	1318(3)	7989(3)	8089(2)	81
H(8)	1541(3)	7922(3)	6095(2)	70
H(9)	2612(3)	7950(3)	4823(2)	85
H(10)	3710(3)	6374(3)	4329(2)	85
H(11)	3678(3)	4786(3)	5077(2)	81
H(12)	2620(3)	4754(2)	6344(2)	70
H(14)	994(3)	5570(3)	9325(2)	89
H(15)	2228(5)	4694(3)	10590(3)	120
H(16)	4201(5)	4127(3)	10492(3)	128
H(17)	4952(4)	4450(3)	9110(4)	124
H(18)	3721(3)	5322(3)	7815(3)	89
H(20)	4139(3)	7207(2)	6766(2)	74
H(21)	5390(3)	5491(3)	6635(2)	87
H(22)	7347(3)	4815(3)	7060(2)	86
H(23)	8051(3)	5862(3)	7622(2)	79
H(24)	6782(3)	7581(2)	7784(2)	64
H(26)	1701(3)	9825(2)	7042(2)	70
H(27)	455(3)	10476(3)	5759(3)	85
H(28)	1189(4)	10642(3)	4339(3)	89
H(29)	3167(4)	10150(3)	4209(2)	88
H(30)	4406(3)	9487(2)	5480(2)	71
H(32)	2693(3)	10452(2)	8543(2)	70
H(33)	1640(3)	10329(3)	9800(2)	82
H(34)	1751(3)	8687(3)	10531(2)	84
H(35)	2891(3)	7158(3)	9991(2)	81
H(36)	3925(3)	7278(2)	8712(2)	66
H(37A)	5820(3)	11730(3)	6731(3)	92
H(37B)	4843(3)	12897(3)	6716(3)	92
H(38A)	4799(3)	12346(3)	5348(3)	92
H(38B)	4522(3)	11400(3)	5884(3)	92
H(39A)	2757(4)	12029(3)	5115(2)	102

H(39B)	2843(4)	13052(3)	4525(2)	102
H(40A)	1161(4)	14148(3)	5199(3)	108
H(40B)	889(4)	13440(3)	4631(3)	108
H(41A)	-572(3)	13163(3)	5428(3)	109
H(41B)	-658(3)	14068(3)	5943(3)	109
H(42A)	-1401(3)	12867(3)	6750(3)	106
H(42B)	-111(3)	11954(3)	6857(3)	106
H(43A)	-227(4)	11815(3)	8433(3)	115
H(43B)	-1445(4)	12818(3)	8392(3)	115
H(44A)	-438(4)	13682(3)	8998(3)	111
H(44B)	-495(4)	12703(3)	9686(3)	111
H(45A)	1176(4)	12504(3)	10460(3)	109
H(45B)	1389(4)	13386(3)	9753(3)	109
H(46A)	3149(4)	12117(3)	10505(2)	111
H(46B)	2973(4)	11199(3)	10164(2)	111
H(47A)	4648(4)	10732(3)	9235(3)	107
H(47B)	4961(4)	11474(3)	9733(3)	107
H(48A)	4902(3)	12576(3)	8325(3)	98
H(48B)	5880(3)	11400(3)	8388(3)	98